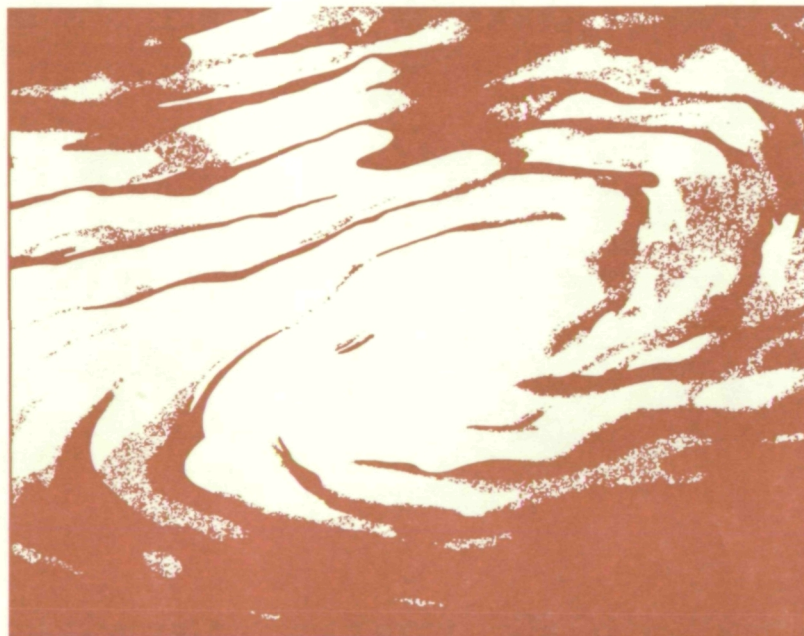


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MECA WORKSHOP ON  
**THE EVOLUTION OF THE MARTIAN  
ATMOSPHERE**



**MECA**

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MECA WORKSHOP ON  
THE EVOLUTION OF THE MARTIAN ATMOSPHERE

Edited by  
Michael Carr, Philip James, Conway Leovy,  
Robert Pepin, and James Pollack

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# Program

Friday, August 9, 1985  
9:00—12:30

## SESSION I—VOLATILE INVENTORY

K. Goettel  
*Rigorous constraints on the bulk composition and volatile inventory of Mars*

R. Pepin  
*Volatile inventory of Mars*

J. Yatteau  
*Mars: Atmospheric escape of major volatiles*

T. Owen  
*Update of the Anders-Owen model for martian volatiles*

J. Pollack  
*Update of the Pollack-Black model for martian volatiles*

2:00—5:45

H. Wänke  
*Can a high abundance of moderately volatile and even some highly volatile elements on Mars be reconciled with its low abundance of primordial rare gases?*

G. Dreibus  
*Comparison of Cl/Br and Br/I ratios in terrestrial samples and SNC meteorites*

R. Huguenin  
*Accreted H<sub>2</sub>O inventory on Mars*

J. Lewis  
*Early volatile element inventories on Mars*

T. Ahrens  
*Accretional constraints on Mars' volatile budget*

H. Watkins  
*Evolution of the atmosphere of Mars as the result of asteroidal and cometary impacts*

P. Schultz  
*The martian atmosphere before and after the Argyre impact*

Saturday, August 10, 1985  
8:30—12:00

## SESSION II—EVOLUTION OF THE ATMOSPHERE

J. Walker  
*Early evolution of the terrestrial atmosphere*

G. North  
*Terrestrial paleoclimate modeling*

R. Kahn  
*The evolution of CO<sub>2</sub> on Mars*

J. Spencer

*Valles Marineris as karst: Feasibility and implications for martian atmospheric evolution*

J. Pollack

*Greenhouse requirements for early dense atmospheres*

1:30—5:00

M. Carr

*Climatic implications of channels*

J. Gooding

*Martian weathering products: Response to climate changes and effects on volatile inventories*

C. Leovy

*Present atmosphere: Evolutionary implications*

A. Zent

*Near-surface ice and brines on Mars*

D. Paige

*Non-linear frost albedo feedback on Mars: Observations and models*

L. Martin

*Major dust storm activity, and variations in the recessions of Mars' south polar cap*

B. Jakosky

*Reversible and irreversible changes in martian climate*

## Workshop Summary

The first day of the workshop focused on the past and present volatile inventory of Mars, and the evolution of this inventory from its primordial to current state through the interplay of gain and loss mechanisms involving volatile sources and sinks both interior and exterior to the planet. Models of the bulk composition of a planet are needed to assess its full complement of volatile species, and K. Goettel, in the leadoff talk, stressed the importance of the observed martian mean density and moment of inertia factor in constraining such models. He pointed out that these geophysical constraints are satisfied (although not uniquely so) by a bulk composition model in which the major rock-forming elements are present in solar (C1) proportions and that this composition is interestingly similar to that derived by Wänke and Dreibus from SNC meteorite data. Goettel, arguing from nebular temperature considerations, also introduced a theme that was later emphasized by J. Lewis, H. Wänke, and other speakers: *Mars; initially, was almost certainly a very volatile-rich planet*. Since abundances of martian atmophilic volatiles are at present very low, this implies large-scale losses of primary atmospheric gases in the past and, within the total volatile inventory of the planet, a decoupling of the abundances of highly volatile atmophilic components, such as the noble gases, from abundances of moderately volatile or condensible gaseous species. This central question of martian atmospheric evolution was addressed, with consideration of a variety of possible processes for both atmospheric escape and atmospheric accretion, in several of the subsequent papers.

If the SNC meteorites come from Mars, then they provide a means of assessing elemental abundances on the planet. R. Pepin compared the abundances of noble gases, nitrogen, and carbon dioxide trapped in glassy phases of the EETA 79001 shergottite with the composition of the martian atmosphere measured by Viking, and he argued that the close elemental and isotopic correspondence of the two data sets warranted at least a working hypothesis of martian origin. He noted that the more precise EETA 79001 data indicate a simple fractionation relation between relative elemental abundances of noble gases in the martian and terrestrial atmospheres. This suggests a common noble gas elemental composition in the primordial reservoir(s) for the two planets, which was subsequently fractionated to a greater extent for Mars than for Earth. The process(es) governing this additional mass-dependent gas loss from Mars relative to Earth is unclear. It seems unlikely that the simple fractionation mechanisms used by Pepin to illustrate the fractionation relation and the ways in which pre-loss abundances might be calculated would actually have operated in planetary environments. In discussions of this point, J. Walker suggested the possibility of noble gas fractionation during hydrodynamic blowoff of an H<sub>2</sub>-rich early martian atmosphere; he and others are now considering this mechanism analytically.

Gases are also escaping from the present martian atmosphere. Current losses of H, O, C, and N were addressed by J. Yatteau in the next paper. All four are escaping at significant rates, and Yatteau predicted that future measurements more accurate than Viking's will find isotopic enrichments in H, O, and C. The large enrichment of <sup>15</sup>N observed by Viking (<sup>15</sup>N/<sup>14</sup>N about 60% above the terrestrial ratio) may be used to infer initial N<sub>2</sub> abundances and evolutionary scenarios, but Yatteau emphasized that these interpretations of current isotopic abundances are sensitive to model assumptions about the initial nitrogen isotopic compositions and the presence or absence of nitrogen sources (e.g., flux into the atmosphere from degassing) and losses other than atmospheric escape (e.g., to surface sinks). A particularly interesting point made by Yatteau in discussing atmospheric evolutionary histories was that if nitrogen was ever more abundant than carbon dioxide, oxygen at that time had to be significantly higher than at present, perhaps even the dominant atmospheric constituent.

The emphasis of the workshop discussions returned more explicitly to the primordial volatile inventory of Mars and to the sources, generation, and evolution of its early atmosphere in a group of talks by J. Lewis, T. Ahrens, and H. Watkins. The magnitude of the initial volatile inventory deduced from models of condensation and accretion in the vicinity of Mars led Lewis to conclude that the martian atmosphere has suffered severe loss of mass. Watkins presented results of his work with Lewis on impact-driven



explosive blowoff, which suggest efficient stripping of atmospheric mass by momentum transfer during energetic impacts. Atmospheric erosion by this process could have continued at lower rates beyond the period of late heavy bombardment; this may be important in assessing the planetary budget of radiogenic noble gases from even long-lived parents (e.g.,  $^{40}\text{Ar}$ ). These Watkins-Lewis calculations do not yet include contributions to the atmospheric inventory by volatiles carried into the system in the impacting bodies. Ahrens stressed the importance of this source in Mars' overall volatile budget. His scenarios of atmospheric evolution, based in part on measurements of degassing in laboratory shock experiments, include generation of an atmosphere by impact devolatilization of chondritic planetesimals during accretion of the planet, as well as losses by atmospheric cratering. The net result for Mars, on the assumption of only a small fraction of the total accreted planetary mass in the form of carbon and water-rich planetesimals, is cogeneration during accretion of a primordial atmosphere containing about 10% of the Earth's carbon dioxide inventory.

Because Mars formed further from the Sun, where temperatures were cooler than where Earth formed, there is good agreement that the Mars-forming planetesimals were rich in volatiles, including water. G. Dreibus presented data from SNC meteorites in support of this view. She showed that in the SNC meteorites (and by inference in Mars) the moderately volatile element Br is three times more abundant with respect to the refractory La than it is in the Earth. However, there is a dispute about how well Mars retained some of these volatiles during the accretion process. On the one hand, Wänke advocates that Mars lost almost all of its initial water endowment. He described a model, based on SNC meteorite abundances, by which Mars was accreted homogeneously from two primary components, a highly reduced volatile-poor component, rich in metallic iron, and a highly oxidized, volatile-rich component. Most of the water is lost from the planet during and immediately subsequent to accretion by reaction with metallic iron followed by escape of the product  $\text{H}_2$ . In contrast, Huguenin argued, on the basis of the composition of minerals on the martian surface as inferred from visible and near-infrared spectral data, that Mars retained much of its initial water inventory as hydrated minerals in the planet's interior. J. Walker cautioned that non-noble gas volatiles such as C, N, and H do not necessarily behave as a group, nor does coherence on one planet imply coherence on another. He pointed out that much of the Earth's inventory of C may have initially existed as very refractory elemental carbon in a highly reduced mantle. Its release, he suggested, may have been controlled by progressive oxidation of the mantle by subducted material. Carbon may thus have had a quite different outgassing history from hydrogen and nitrogen, so use of terrestrial C/H and C/N ratios to assess volatile inventories on Mars may be questionable.

There are also major controversies concerning the importance of external sources of volatiles for Mars and the other terrestrial planets. Attempts to explain the inert gas contents of the atmospheres of the terrestrial planets fuel much of the controversy. Key external sources include the solar wind (which is particularly relevant for the inert gases possibly gained by Venus), asteroids (a potential source of  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$  but not inert gases), and comets (a potential source of  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ , and the heavier inert gases). As pointed out by Owen, water ice may be able to quantitatively incorporate C- and N-containing gases and the heavier inert gases (but not He and Ne) into its crystal structure at the low temperatures where the comets formed. If so, the C/N ratio in their volatile inventories far exceeds the solar abundance value. Owen advocates a unique collision of Venus with a very large comet as a way of explaining its large inert gas content (with the solar wind as the principal Ne source) and large losses from Mars' early atmosphere as a means of depleting its inert gas content. On the basis of the K/U abundance in SNC meteorites, Pollack and Black infer that  $^{40}\text{K}$  bulk abundance (per gram of planet) is about the same for Mars as the Earth and hence the factor of 16 depletion in  $^{40}\text{Ar}$  in the martian atmosphere (per gram of planet) is due in part to the loss of some of the early atmosphere of Mars—the remainder is due to less efficient outgassing. Pollack and Black also still favor their grain adsorption model as the source of the inert gases in planetary atmospheres, but suggest that adsorption in the gravitationally enhanced high density region around forming planets may represent an easier means for incorporating the required amounts of inert gases.

Evidence for the evolution of martian climate from an early warm relatively moist regime to the present dry cold regime, or evidence of transient warm episodes within the past 2 or 3 billion years, may be sought in the surface geomorphology and geochemistry. The origins of Mars' well-known channels remain unclear. The outflow channels appear to be the most unambiguously fluvial. They appear to have been produced by floods, possibly arising from local release of groundwater or mobilization of water as a result of local volcanic heating. They probably could form under a wide range of climatic conditions, including those at present, and therefore do not necessarily indicate climatic fluctuations. The other major channel class, the branching valley networks, is generally associated with very ancient terrain. While these channels are widely believed to have been produced during a warmer wetter regime, M. Carr discussed the possibility that they formed from meltwater accumulated at the base of a snow pack under climatic conditions only moderately warmer than at present. The snow pack could have accumulated periodically at low latitudes when obliquities were very high. Wind erosion and deposition patterns might also be indicative of climatic change. Evidence for extended periods of intense aeolian modification of the surface within the past 3.5 billion years or so is lacking. On the contrary, the preservation of small-scale surface features that evidently date back to very early times argues against such aeolian episodes. This is significant, because any extended period of greatly increased atmospheric pressure should have been accompanied by enhanced aeolian modification of the surface almost everywhere. Like the branching valley networks, intense aeolian modification of the surface seems to have been restricted to a very early period.

A detailed survey of the morphology of large impact basins suggests a transition in both the mechanism of ejecta emplacement and the rate of formation of branching valley networks at about the time of the formation of the Argyre basin, late in the heavy bombardment period. P. Schultz showed that, prior to that event, the geomorphological evidence indicates that the atmosphere was much more massive and may have been capable of sustaining a climate that could produce surface runoff.

R. Kahn showed that if there was an early moist episode in martian climatic history, as the branching valley networks and evolution in morphology of impact basins suggest, then  $\text{CO}_2$  would have reacted in liquid water to form carbonates, ultimately reducing the atmospheric pressure and terminating the conditions under which liquid water could exist at the surface. He proposed that the similarity in the present  $\text{CO}_2$  pressure at the surface and the pressure at the triple point of  $\text{H}_2\text{O}$  is not a coincidence but a direct result of this process. Spencer and Croft pointed out that if large amounts of  $\text{CO}_2$  have been lost from the atmosphere, then large near-surface deposits of carbonates are to be expected. An active groundwater system interacting with such massive surface carbonate deposits could have produced certain collapse features and portions of the martian equatorial canyon system. This might account for some unexplained aspects of these topographic features, but the maintenance of a groundwater system adequate to the task is difficult to explain. Observational evidence for carbonate deposits would be of great value, but is difficult to obtain with remote-sensing techniques, and a convincing detection of carbonates is still lacking.

A few papers dealt with the current atmosphere and volatile cycles on Mars and variations in these on time scales ranging from several annual cycles to periods of  $10^3$  to  $10^6$  years, characteristic of the astronomical cycles of orbital parameters. C. Leovy introduced the topic with a review of the present knowledge of the current martian atmosphere and discussed the implications for the evolution of the climate. The nature and size of volatile reservoirs remain as one of the major uncertainties that impede extrapolations to past climate regimes. Two papers were presented that described new models for portions of the  $\text{H}_2\text{O}$  and  $\text{CO}_2$  volatile cycles. A. Zent reported on a model being developed by F. Fanale and himself that considers the detailed interactions between water in its various phases and the regolith. Their preliminary results suggest that the adsorptive capacity of the regolith determines the phase of  $\text{H}_2\text{O}$  in the surface layers but that the total amount of  $\text{H}_2\text{O}$  exchanged is relatively independent of the adsorptive capacity. D. Paige discussed a model, developed by himself and H. Kieffer, that incorporates the monotonic dependence of  $\text{CO}_2$  ice albedo on the insolation observed in Viking IRTM data. The preliminary results

indicate that the current seasonal pressure wave is adequately reproduced; the response of the model to astronomically induced insolation variations is quite different from the variations predicted by previous models. In the final paper in the session, L. Martin presented an analysis of pre-1971 photographic data; the objective of the project is to discover whether significant interannual differences occur in the regression of the south polar cap. A preliminary comparison of 1956 and 1971 data suggests that such variations do occur.

# ABSTRACTS

## ACCRETIONAL CONSTRAINTS ON MARS' VOLATILE BUDGET; Thomas J.

Ahrens, Seismological Laboratory 252-21, California Institute of Technology, Pasadena, CA 91125

Although the present atmospheric and visible H<sub>2</sub>O budgets of Mars are extremely small both ancient erosional land forms and consideration of the physics of accretion and cogeneration of an impact produced atmosphere indicates that Mars has lost little H<sub>2</sub>O and virtually no CO<sub>2</sub> during its formation from a chondritic assemblage silicate and iron-bearing planetesimals. Most of the water loss is by atmospheric cratering on Mars. If Mars, like the earth, has a nearly chondritic D/H ratio, it follows that most of the water delivered to the planet was in the form of phyllosilicate matrix phases such as bear the preponderance of water in carbonaceous chondrites. Following Arrhenius et al. (1974) and Lange and Ahrens (1982) we assume that the impact dehydration of serpentine:



delivers most of the water to a coaccreting planetary atmosphere. Experiments demonstrate that shock pressure of ~20 GPa, or infall velocities of greater than ~1.5 km/sec are required to devolatilize serpentine. This infall velocity corresponds to a proto-Mars which has grown to only 0.4 of its final radius. Experiments indicate that even at infall velocities of ~5 km/sec (the present escape velocity) reaction (1) will only achieve some 80% dehydration of planetesimals. A CO<sub>2</sub> budget in the atmosphere and crust is assumed to also form as a result of the following chain of reactions:



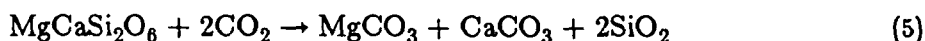
occurring in the atmosphere and



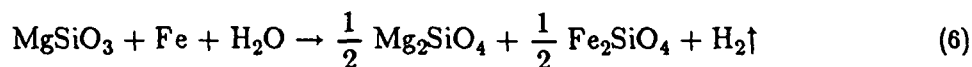
occurring upon impact of graphite-bearing planetesimals, not unlike the C in carbonaceous chondrites. Also hydrocarbons, such as CH<sub>4</sub>, are likely to also be oxidized and form CO<sub>2</sub> upon impact via reactions such as



Finally, we expect that under sufficiently low temperatures, on Mars, carbonates will provide a near surface reservoir of CO<sub>2</sub> from the Urey reaction.



Using the results of shock recovery experiments on CaCO<sub>3</sub> and Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> and atmospheric accretional calculations, starting with the terrestrial planets having initial surface radiation temperatures of 218, 253, and 390 K for Mars, Earth, and Venus the evolution of radiation heat loss controlled atmosphere may be calculated using the results of O'Keefe and Ahrens (1982) to calculate atmospheric cratering losses. It is assumed that both CO<sub>2</sub> and H<sub>2</sub>O are produced via reactions 1-4 and H<sub>2</sub>O is lost upon conversion to H<sub>2</sub> either via reaction 2 or via the surface reaction:



By assuming that the fraction of carbon and water-bearing material for Mars, Earth and Venus was only 0.4% and this consisted of 93% H<sub>2</sub>O-bearing material, Mars is found to end up with 10<sup>23</sup> g of CO<sub>2</sub> in its primordial atmosphere at a surface temperature of 610K or about 0.1 of the earth's CO<sub>2</sub> (Ruby) budget. In contrast Venus has a 10<sup>24</sup> g CO<sub>2</sub> atmosphere and a 0.4 x 10<sup>24</sup> g H<sub>2</sub>O budget in the atmosphere, with a surface temperature of 1100K. The fixed point in such models is the earth, which retains 1.2 oceans in the atmosphere and a Ruby budget of CO<sub>2</sub> in a primordial atmosphere with a surface temperature of 683 K.

## MARS' VOLATILES

Ahrens, T. J.

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CLIMATIC IMPLICATIONS OF MARTIAN CHANNELS. Michael H. Carr. U. S. Geological Survey, Menlo Park, CA 94025

Channels incised into the martian surface have been widely cited as evidence that, at various times in its history, Mars has experienced climatic conditions substantially different from those that presently prevail. The arguments are based on two assumptions: 1) the channels formed by fluvial erosion, and 2) fluvial erosion requires surface temperatures above freezing. Atmospheric pressures in excess of 2 bars may be required to achieve surface temperatures in excess of 273°K (1). Eolian erosion and depositional rates higher than those at present are expected from such thick atmospheres but preservation of very old, fine, surface features suggests erosional and depositional rates on Mars have been very low - comparable to those on the Moon - throughout martian history. It is pertinent, therefore, to examine the validity of the two suppositions that lead to consideration of a thick atmosphere.

Outflow channels present the most compelling evidence of fluvial erosion. They have numerous characteristics in common with large terrestrial flood features. However, large floods could form under present climatic conditions. Indeed, if they form by breakout from confined aquifers (2) then a thick permafrost and climatic conditions similar to those that presently prevail are required. Formation of branching valley networks may be more sensitive to climate since they appear to have formed by slow erosion rather than catastrophic floods. Their pattern of dissection crudely resembles that of terrestrial river valleys in that tributaries feed larger trunk streams. However, tributaries are few, interfluves are undissected, drainage basins are not contiguous, channels have not been identified within the valleys, and distances from the start of the most distant tributary to termination of the trunk stream are short. Whatever the erosive mechanism, it was very inefficient, having affected only a minute fraction of the surface. Most of the valleys appear to be very old, being mostly restricted to the old cratered highlands.

On the unproven supposition that the valleys were formed by running water, the climatic sensitivity of several aspects of stream initiation and stability have been examined. If the atmospheric pressure is less than 2 bars ambient temperatures will be below 273°K and a stream will freeze. Rates of freezing were calculated for atmospheric pressures ranging from 7 mb to 1 bar by assuming the globally averaged temperatures of Pollack (1) and balancing solar and infrared incident radiation on the streams surface against radiative and evaporative heat losses, and conductive heat losses to both atmosphere and ground. From the hydraulics of stream flow, the distance that various sized streams could flow before flow was arrested by freezing, was then calculated for different conditions. Results indicate that stream stability is relatively insensitive to atmospheric pressure until pressures are so high (1-2 bars) that the ambient temperature approaches 273°K. A stream 1-2 meters deep could survive long enough to flow tens of kilometers even with atmospheric pressures in the 10-100 mb range.

A stream can be initiated either by precipitation or groundwater seepage. If temperatures are below freezing, precipitation will be as ice. This could follow as a result of injection of large amounts of water into the atmosphere by large impacts, or as a consequence of equatorial transportation of water vapor evaporated from the summer poles during periods of high obliquity (3). Because snow is translucent and has a low thermal conductivity, melting temperatures can occur within a snowpack even when

surface temperatures are well below freezing (4). The amount of melt, if any, depends on a variety of factors including surface temperature and pressure, the thermal conductivity, density, albedo and dust content of the snow, the thermal properties of the soil on which the snow sits, and local winds. For mature, coarse grained snow with a dust content of 1000 ppm by weight, melting can occur when atmospheric pressures are as low as 30 mb. Whether sufficient melt can accumulate at the base of the snow pack and collect into streams and erode the valleys remains to be demonstrated.

Several characteristics of the martian channels suggest origin by groundwater sapping (5). A thick permafrost currently inhibits sapping. The permafrost would be thinner, and sapping more probable, if surface temperatures were higher and heat flows larger. Very early in Mars history heat flows may have been significantly higher (6), thereby facilitating sapping, but the climatic constraints are yet to be determined.

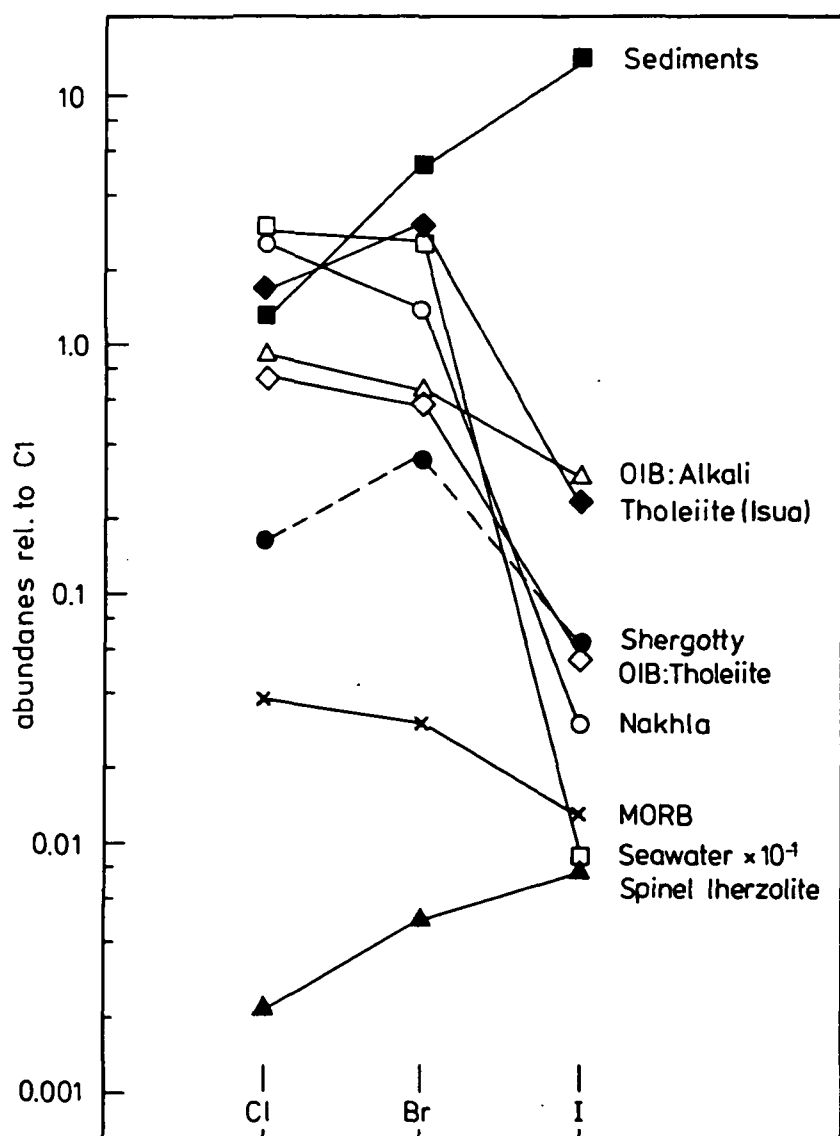
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COMPARISON OF Cl/Br AND Br/I RATIOS IN TERRESTRIAL SAMPLES AND SNC METEORITES. G. Dreibus and H. Wänke, Max-Planck-Institut für Chemie, Saarstrasse 23, D-6500 Mainz, F.R.Germany.

We have previously tried to estimate the halogen content of Mars on the assumption that SNC meteorites (Shergottites, Nakhrites, and Chassigny) are indeed of Martian origin (Wänke and Dreibus, 1984). The Consortium studies on Shergotty meteorite (J.C. Laul Consortium Leader) yielded the first reliable data for iodine in addition to F, Cl and Br in a shergottite. The shergottites EETA 79001-B and ALHA 77005 like other meteorites found in Antarctica show a high contamination of iodine and to a lesser degree of Cl whereas EETA 79001-A and the glass inclusion from EETA 79001 are uncontaminated (Dreibus and Wänke, 1985).

The determination of halogens in the EETA 79001-glass sample in which Bogard and Johnson (1983) have discovered trapped noble gases with elemental and isotopic ratios similar to those measured in the Martian atmosphere gives a low I concentration of  $0.012 \pm 0.004$  ppm and compared to the surrounding matrix a



similar Cl concentration and a twofold excess of Br. In this glass-sample Becker and Pepin (1984) observed an  $^{80}\text{Kr}$  and  $^{128}\text{Xe}$  enrichment of about 10 compared to the surrounding matrix. However as we could not find a corresponding enrichment of the target elements  $^{79}\text{Br}$  and  $^{127}\text{I}$ , neutron irradiation cannot have occurred in the EETA 79001 meteoroid itself as already suggested by Becker and Pepin (1984).

The absolute concentrations obtained for Shergotty are: F = 41 ppm; Cl = 108 ppm; Br = 0.89 ppm, and I = 0.036 ppm. High Br/I and Cl/I ratios (normalized to C 1) of 6, respectively 2.5, also found for the EETA 79001-glass, indicate depletion of I relative to Br and Cl.

A similar depletion of I is observed in a large number of terrestrial basalts as shown in the Figure.

However, the bulk Earth Br/I ratio may be chondritic, since the major fraction of terrestrial I is contained in sediments while the ocean water is the main reservoir of Br and Cl. Consequently in the terrestrial ocean water iodine is depleted relative to Cl and Br and the Cl abundance by a factor of 300. In samples from the Earth's mantle, i.e. spinel and garnet lherzolites we do not find an I depletion relative to Br and Cl. Among igneous rocks the largest depletion of I relative to Br and Cl and Cl abundance are found for tholeiites from ocean island (OIB) as well as from Isua-region (depletion 10x). MORB-samples and alkali basalts from ocean island have only small iodine depletions. Because of the strong iodine depletion in the terrestrial ocean water, it seems likely that the depletion observed for various terrestrial rocks is somehow related with seawater or seawater derived salt deposits. Similar processes on the SPB may have established the observed I depletion in Shergotty. It can, of course, not be excluded that a high Br/I ratio is characteristic for the whole parent planet.

From the Br-La correlation observed for shergottites as well as for terrestrial basalts which couples the volatile element Br to a refractory element La, we conclude that Mars as SPB (Shergotty parent body) has absolute Br concentration exceeding that of the Earth by about a factor of 3.8. In other words, the absolute Cl and Si normalized abundance of Br for Mars is found to be 0.034 compared to a terrestrial bromine abundance of 0.0090.

In light of the high chlorine abundance in the Martian soil (Clark et al. 1977), it is interesting that we found in one of the SNC meteorites, namely Nakhla, extraordinary high concentrations of Cl and Br (Cl = 1891 ppm; Br = 3.46 ppm), but only a small amount of iodine (0.017 ppm). The I depletion in Nakhla relative to Cl and Br and the Cl abundance yields a factor of 75. As most of the Cl and Br and also most of the sulfates and carbonates in Nakhla are water-leachable, we cannot exclude terrestrial contamination.

However, we like to underline that such anomalous high Cl and Br contents have never been observed in any other meteorite not even in the highly Cl and I contaminated meteorites recovered from Antarctica. Nakhla is an observed fall and we found similarly large Cl and Br concentrations in three different samples of Nakhla coming from different collections. On the other hand, Bunch and Reid (1974) reported the discovery of iddingsite in Nakhla indicating hydrothermal alteration of olivine. Hence, the high Cl and Br contents could also be the result of infiltration of a brine on its parent body.

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RIGOROUS CONSTRAINTS ON THE BULK COMPOSITION AND VOLATILE INVENTORY OF MARS. Kenneth A. Goettel (Dept. of Geological Sciences, Brown University, Providence, RI 02912)

The bulk compositions of the terrestrial planets are constrained in part by rigorous bounds derivable (to varying degrees for each of the planets) from geophysical data and from chemical data obtained in situ or by remote sensing. In part, however, the bulk compositions are constrained only by the inferred plausibility of assumptions made about the processes responsible for producing planets. Such inferred "constraints" are highly subject to varying interpretations depending on the predilections of the interpreter. Present data are consistent with Venus, Earth, and Mars all having solar (i.e., C1 chondritic) ratios of the major non-volatile elements. Differences in composition between these planets are relatively small, but very significant with respect to some aspects, including volatile inventory.

The composition of Mars is constrained rigorously by the observed mean density and moment of inertia factor of the planet. These constraints, however, are insufficient to specify the composition uniquely. The range of zero pressure Martian mantle densities and core sizes which are compatible with the mean density and moment of inertia factor were explored by:

- a) considering the full range of plausible core compositions, and
- b) investigating the sensitivity of computed mantle densities to uncertainties in the input parameters (Goettel, 1981). The zero pressure density of the Martian mantle is estimated to be  $3.44 \pm 0.06 \text{ g/cm}^3$ .

The mantle density and core sizes derived by Goettel (1981) are compatible with Mars being composed of solar proportions of the major rock forming elements, with approximately 30% of the total iron in Mars present as FeO (Goettel, 1983). The composition calculated solely on the basis of solar proportions gives a bulk composition of Mars which is very similar to the composition derived by Wanke and Dreibus (1985) from petrologic modeling of the parent body of SNC meteorites. The geophysical constraints on mantle density and the petrologic inferences drawn from SNCs indicate that the mantle of Mars is enriched in FeO by about twice the terrestrial value.

If temperature were the dominant determinant of volatile retention in materials accreting to form planets, then the initial volatile inventory of Mars should have been  $\geq$  the initial volatile inventory of Earth. This conclusion holds virtually independent of what the volatile retention mechanisms were and virtually independent of the specific bulk composition model for Mars which is adopted. Furthermore, this conclusion applies to all volatile species, including FeO, FeS, alkali metals, Tl and other moderately volatile metals, H<sub>2</sub>O, carbonaceous and nitrogenous material, and noble gases. The evidence for temperature being the dominant determinant of volatile retention includes: the gross trends of chemical composition exhibited by solar system objects, nebular models which have temperature decreasing with heliocentric distance, and the rigorously derived differences in bulk composition between Mars and Earth (e.g., the FeO content of their planetary mantles).

The oxidation of Fe metal to FeO is a low-temperature process and it is difficult to envision a process by which oxidation of Fe would proceed to a greater degree in the materials constituting Mars than for Earth without also resulting in greater retention of other volatile species in the Mars

materials. This conclusion holds whether the oxidation of Fe occurred in the nebula (reaction of  $H_2O$  with Fe) or in a planetary body (addition of low-temperature oxidized material to less volatile-rich, more reduced material).

My principal conclusions are: 1) the initial volatile inventory of Mars was equal to or substantially greater than that of the Earth for all volatile species, 2) the enrichment factor for Mars/Earth increases with increasing volatility (i.e., highly volatile species may be depleted in the Earth) and 3) partial melting, planetary differentiation, degassing, and volatile evolution occurred primarily during the accretion process. Future work necessary to evaluate the volatile inventory and history of Mars includes: deriving more rigorous bounds on bulk composition and initial volatile inventory from geophysical constraints and SNC modeling, reassessing the thermal and tectonic evolution of Mars in the context of differentiation (during accretion) of a very volatile-rich planet. Finally, quantitative evaluation of possible loss mechanisms for volatiles is essential for understanding the volatile evolution and present volatile inventory of Mars.

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MARTIAN WEATHERING PRODUCTS: RESPONSE TO CLIMATE CHANGES AND EFFECTS ON VOLATILE INVENTORIES. J. L. Gooding, SN2/Planetary Materials Branch, NASA/Johnson Space Center, Houston, TX 77058 USA.

Introduction. Products of chemical weathering on Mars should serve not only as passive indicators of the climate(s) in which they formed but also as active participants in the cycling and storage of volatiles. Effects of dust particles on atmosphere/surface heat balance and on heterogeneous nucleation of condensates might vary significantly with the age or climatological provenance of the dust. In contrast with pulverized primary, igneous minerals, secondary mineral(oid)s exhibit substantial ranges in key properties, including total specific surface area (for a given particle size), heat capacity, water-complexation ability, and gas-sorption selectivity. A regolith dominated by secondary mineral(oid)s might produce significant elemental and isotopic fractionations between surface and atmosphere as a consequence of volatile/regolith interactions. Critical Issue #1: Availability of Liquid Water. Abundance and longevity of liquid water should largely control the pathways of Martian weathering. Generally Earth-like processes and products are expected for liquid-solid reactions whereas gas-solid conditions (controlled by water-vapor abundance) might lead to highly selective reactions and a dearth of hydrous products [1]. On Mars, instability of liquid water (i.e., relative to ice) is mostly due to low temperature because the problem of low atmospheric pressure (i.e., instability relative to vapor) can be overcome, at least temporarily, by overburdens of dust [2], even without intervention by brine-forming salts. Thin films of unfrozen, interfacial water can exist in porous rocks and soils at sub-freezing temperatures although, in the current Martian temperature regime, film thicknesses would be only 1-2 molecular layers [3]. For a porous igneous rock, existence of interfacial water in a thermodynamically "liquid" thickness ( $\geq 15$  molecular layers) is estimated to occur at  $\geq 263$  K [4]. Therefore, climatically controlled changes that elevate temperatures to near the freezing point, even without exceeding it, might stimulate the critical transition from gas-solid to liquid-solid weathering. Critical Issue #2: Clay Minerals vs. Clay Mineraloids. Formation of well-crystallized clay minerals is favored by slow precipitation from alkaline water that contains previously dissolved Si, Al, and other ions whereas less favorable conditions generally yield cryptocrystalline mineraloids [5]. Under Mars-analogous conditions on Earth, low-temperature weathering of basalts leads to formation of palagonite and related mineraloids [6] although crystalline clay minerals are common products of hydrothermal alteration of melt-rock and breccia at impact craters [7]. Crystalline clay minerals are well-known adsorbents and, if present on Mars, should have a profound effect on retention of volatiles by the regolith [8]. Furthermore, low-temperature, aqueous diagenesis should lead to increased  $^{18}\text{O}/^{16}\text{O}$  ratios but decreased D/H ratios in clay minerals relative to water [9]. Although carbon isotopic fractionations might be controlled mostly by carbonate-forming reactions,  $^{13}\text{C}/^{12}\text{C}$  fractionations might also arise by repeated adsorption and desorption of  $\text{CO}_2$  on clay minerals and further  $^{18}\text{O}/^{16}\text{O}$  fractionations might occur during oxygen exchange between adsorbed  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Indeed, the  $\text{CO}_2/\text{H}_2\text{O}$  fractionation factor for  $^{18}\text{O}$  is 1.041 at 298 K [10] (cf., 1.027 for montmorillonite/water [9]) but should be even larger at Martian temperatures. Because nitrogen is effectively inert, fractionation of  $^{15}\text{N}/^{14}\text{N}$  by adsorption on clay minerals should be relatively small, though perhaps still worthy of investigation. As dust particles in the Martian atmosphere, nonexpandable clay minerals (or expandable clay minerals in highly

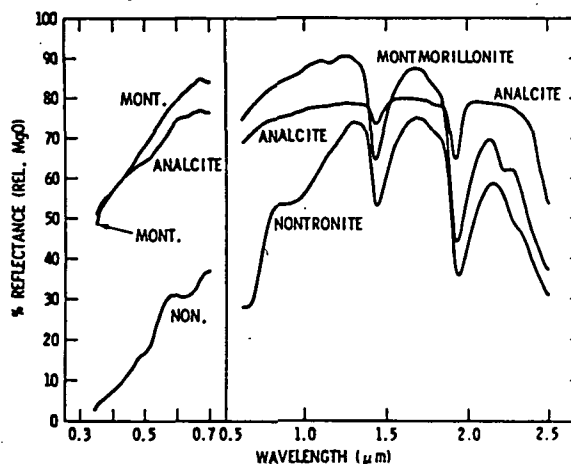
## WEATHERING PRODUCTS AS CLIMATE INDICATORS

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desiccated conditions) might favor heterogeneous nucleation (and settling) of  $H_2O$  and  $CO_2$  condensates [11], thereby further enhancing movement of volatiles toward the regolith. However, cryptocrystalline mineraloids are expected to be much less effective condensate nucleators [11].

Although much is known about clay-mineral geochemistry, neither the absorbent properties nor the stable-isotopic systematics are understood nearly as well for palagonite-like mineraloids. If, in fact, crystalline clay minerals are not abundant on Mars [12], the role of the regolith as a volatile sink, both in terms of elements and isotopes, should be different than if clay minerals were major components. Clearly, an important goal in exploration of Mars should be determination of changes in the abundances, identities and degrees of crystallinity of clay mineral(oid)s throughout Martian history. However, distinction between crystalline clay minerals and poorly crystalline clay mineraloids by remote spectrophotometry may not always be definitive [13] so that laboratory analyses of documented samples will be indispensable.

**Critical Issue #3: Zeolites.** In contrast with clay mineral(oid)s, zeolite crystallinity is relatively independent of precipitation conditions and, on Earth, zeolites are major secondary minerals both in weathered basalts and in hydrothermally altered impact melt-rocks and breccias [6,7]. Zeolites are well known as strong absorbents although their molecular-sieve structures make them more selective and tenacious absorbers than are clay minerals [14]. For example, chabazite preferentially absorbs  $CO_2$ , relative to  $N_2$  and  $O_2$ , and, as is the case for various zeolites, absorptivity varies with identity of the structurally interstitial cation (e.g., Na, K, or Ca) [15]. Although zeolites have been selectively utilized in deliberate heavy-isotope separations [16], the behavior of natural zeolites with regard to stable-isotopic fractionations of H, C, N, and O in geologic environments is not well known. However, it is likely that volatiles retained by Martian zeolites will, in general, be enriched in heavy isotopes (with the possible exception of D/H) relative to water or atmospheric gases with which they have reacted. Even so, if correction factors for fractionation effects can be determined, the gas content of a given Martian zeolite might comprise an extremely useful sample of the Martian atmosphere as it existed at the time of zeolite formation. Although gas analyses will require documented samples, spectrophotometry of Mars might facilitate reconnaissance for zeolites, especially among suspended atmospheric dust particles. Some zeolites (e.g., analcite, Fig. 1) might resemble Fe-poor clay minerals (e.g., montmorillonite) in the visible spectrum but near-infrared differences should be greater (e.g., 2.2-2.5- $\mu m$ ). Therefore, in addition to discriminating clay minerals from mineraloids, future remote-sensing of Mars should attempt to distinguish zeolites from clay mineral(oid)s. Because zeolites are expected to be comparatively good nucleators of condensates [11], dust particles that are associated with condensate clouds should be observational targets of special interest.



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ACCRETED H<sub>2</sub>O INVENTORY ON MARS; R.L. Huguenin and S.L. Harris, University of Massachusetts, Amherst, MA 01003

Reflectance spectra of twelve surface areas (~1000km diameter) have been analyzed using a new intelligent absorption band detection algorithm (Huguenin and Jones, 1985). The analysis permitted suites of absorption bands to be detected for the first time in Mars spectra and accuracies of detected band positions revealed the apparent identity of exposed igneous minerals (Huguenin and Anderson, 1985). The findings provided significant constraints on models of planetary composition, oxidation state, and volatile content.

One of the significant findings was that minerals in the broadly distributed areas were similar. Six of the twelve areas had bands that could be attributed to olivine of composition Fo<sub>65</sub>±15. Four areas had bands consistent with the presence of fayalite (iron-rich olivine). Six of the twelve spectra had bands that were attributed to low-iron enstatite. All twelve areas had bands that could be attributed to high-calcium pyroxene, with the pyroxenes in eleven of the twelve areas being high-iron varieties. The pyroxenes were all oxidized with Fe<sub>2</sub>O<sub>3</sub>/FeO ≈ 0.3-3.0%.

The second finding was that the detected minerals were similar to the normative minerals derived from Viking compositional analyses of martian fines with modified Mg (Huguenin and Anderson, 1985). It has been argued that the relative metal abundances of martian fines may represent a globally averaged composition of crustal rocks that have been exposed at the surface over geologic time (Huguenin, 1982). Huguenin et al (1985) modified this proposal with the suggestion that Mg may be preferentially depleted from the fines due to reaction of fines with aerosol sulphate and chlorides derived from brine evaporation. It was argued that aerosols would react principally with Mg<sup>2+</sup> as a result of incipient removal of Fe<sup>2+</sup> from ferromagnesian minerals to form iron oxide, resulting in enhanced susceptibility of Mg<sup>2+</sup> to subsequent reaction. It was argued that the resultant Mg salts would be highly soluble and be dispersed into the planetary hydrosphere, depleting Mg by a factor of 1-10 (Huguenin et al, 1985). Enhancements of Mg in the Viking fines analyses by factors of 2-5 yielded normative mineralogies that were consistent with the detected phases (Huguenin and Anderson, 1985). Results yielded 22-76% normative olivine of composition Fo<sub>61</sub>-Fo<sub>80</sub>, compared to detected Fo<sub>65</sub>±15. Normative high calcium pyroxene abundances ranged from 13%-7% by weight with compositions of Wo<sub>50</sub>, En<sub>30</sub>, Fs<sub>20</sub> to Wo<sub>50</sub>, En<sub>40</sub>, Fs<sub>10</sub>, compared to detected pyroxene compositions of Wo<sub>40-51</sub>, En<sub>22-44</sub>, Fs<sub>6-27</sub>. Normative low-calcium, low-iron pyroxene ranged from 34-0% of Fs<sub>39</sub>-Fs<sub>0</sub>, compared to detected pyroxene of composition near Fs<sub>10</sub>. Minor normative orthoclase (1.7-0%), nepheline (0-3.1%), and magnetite (4.4-2.5%) would not have been detectable. Derived normative plagioclase (An<sub>65</sub>-An<sub>84</sub>) had sufficient abundance (25-10%) to be detected, but absorption by other phases prevented detection (Huguenin and Anderson, 1985). The similarity of detected and normative phases supported the possibility that the detected phases in the 12 analyzed areas may have been representative of crustal minerals over much of the planet. This possible mineralogic uniformity and possible peridotitic composition suggests that the magmas may have been minimally-evolved near-primitive melts (Huguenin and Anderson, 1985).

This possibility is further supported by the comparison shown in Table I. The column on the left shows the average crustal composition that was derived by Huguenin and Anderson (1985). The column in the middle is the mantle and

crust composition that was predicted from the equilibrium condensation and homogeneous accretion model proposed by J.S. Lewis and coworkers (Basaltic Volcanism Study Project, 1981, p.642). The column on the right is the composition for the mantle plus crust derived by Wanke and Dreibus (1984). The three compositions are very similar. The agreement between the first and third columns is expected, since both are based on measured analyses of surface samples from Mars. The similarity of the middle column to the outer two columns is striking, however, since the middle column represents a first-principles modeling of mantle and crust compositions resulting from equilibrium condensation and homogeneous accretion of the planet from the primitive solar nebula. It was based on no prior knowledge of Mars composition. Earlier support for the model was provided by the excellent agreement of predicted and measured geophysical properties (Basaltic Volcanism Study Project, 1981, p.688). Derived planetary mass ( $6.31\text{--}6.32 \times 10^{26}\text{y}$ ) in the Lewis-Weidenschilling model differed from actual mass ( $6.41 \times 10^{26}\text{y}$ ) by only 1.45-1.73%. Derived  $1/MR^2$  (0.3684-0.3682) deviated by less than 1% from the actual value (0.3650).

The agreement of the derived average crustal composition with the two mantle and crust compositional models suggests the possibility that the exposed surface rocks may have virtually indistinguishable composition from the crust plus mantle as a whole. While differentiation may have resulted in core formation, it may not have produced a compositionally segregated crust and mantle. If true, this would be consistent with cold accretion models in which core formation can occur but segregation of a crust by crystal-liquid fractionation would not (Basaltic Volcanism Study Project), 1981, pp.1201-1202).

The agreement further provides a well-supported basis for estimating the abundance of accreted  $\text{H}_2\text{O}$ . From Table I the Lewis-Weidenschilling model predicts that  $\text{H}_2\text{O}$  comprised 0.44-0.47 weight percent of the mantle plus crust. Their model predicts that the mantle plus crust is 71-74% of the total planetary mass, yielding a predicted mass for accreted  $\text{H}_2\text{O}$  of  $2.0\text{--}2.2 \times 10^{24}\text{g}$ . Wanke and Dreibus predicted that accreted  $\text{H}_2\text{O}$  comprised 2.1% of the planet by mass, or  $13 \times 10^{24}\text{g}$ . If all the  $\text{H}_2\text{O}$  were released from the interior and spread uniformly over the surface of the planet ( $1.4 \times 10^8\text{km}^2$  surface area), the Lewis-Weidenschilling mass would be equivalent to a 14-16km thick surface layer of ice. The Wanke-Dreibus mass would be equivalent to a 93km thick layer of ice.

The implications that the mantle plus crust may be compositionally uniform, i.e., that crystal-liquid fractionation and crustal segregation may not have occurred, suggests that the  $\text{H}_2\text{O}$  source minerals may have been relatively uniformly accreted throughout the mantle and crust. The Lewis-Weidenschilling model predicts that the primary  $\text{H}_2\text{O}$  source phases would be talc- and tremolite-family silicates. If the low temperature accretion model is correct, such phases could be stable against dehydration to a depth of  $\sim 300\text{km}$ , except where volcanism and impact produce locally high P-T conditions (Merrill, 1978). The upper 300km of the planet corresponds to  $\sim 1/3$  of the mantle and crust volume, and it is possible that only  $\sim 2/3$  of the accreted  $\text{H}_2\text{O}$  may have been lost from the planet during its early history. The  $\text{H}_2\text{O}$  in the upper 300km could have been largely retained and it may have had significant influence on crustal properties and processes.

The presence of talc- and tremolite-family phases in the upper  $\sim 300\text{km}$  could produce density contrasts that could possibly explain the partial to



complete isostatic compensation of surface topography. Densities (uncompressed) of the dehydrated phases would be near  $3.5 \text{ g cm}^{-3}$ , while the densities of tremolite- and talc-family phases would be closer to  $2.8\text{--}3.2 \text{ g cm}^{-3}$ . Lateral density variations within the upper few hundred kilometers have been proposed as possibly accounting for the observed isostatic compensation (Basaltic Volcanism Study Project, 1981, p.1199). It is thus possible that the principal compositional difference between the crust and mantle is the presence and absence of water of hydration.

Dehydration by impact and volcanism during the late-stage accretion and post-accretionary periods could have released substantial  $\text{H}_2\text{O}$ . Consider a  $1 \times 10^6 \text{ km}^3$  volcanic event, such as Arsia Mons or events in the Olympus-Tharsis Province discussed by Scott (1982). Scott estimated the volume of the Olympus-Tharsis Province to be  $25 \times 10^6 \text{ km}^3$  in more than 15 eruptive episodes, amounting to  $\sim 1.7 \times 10^6 \text{ km}^3/\text{event}$ . Using the Lewis-Weidenschilling estimate of the  $\text{H}_2\text{O}$  content of the source rocks (0.44–0.47% by weight), a  $1 \times 10^6 \text{ km}^3$  volcanic event would release  $1.3\text{--}1.6 \times 10^4 \text{ km}^3 \text{ H}_2\text{O}$ . If all of the  $\text{H}_2\text{O}$  were deposited at the poles (1000km diameter area in the north and 350km diameter area in the south), a  $1 \times 10^6 \text{ km}^3$  event could deposit 15–18m layers of ice at each pole. Release of  $\text{H}_2\text{O}$  by volcanism and impact from the upper 1km of regolith over time could result in the deposition of 2.1–2.4km thick layers of  $\text{H}_2\text{O}$  at the two poles, enough to comprise 37–67% of the present cap volumes (4–6km thick at the north and 1–2km thick at the south assumed). Dehydration that accompanied development of an equivalent  $\sim 1\text{km}$  thick layer of flood basalts, volcanic shields, and impact material could thus possibly have released enough  $\text{H}_2\text{O}$  to account for the estimated volumes of  $\text{H}_2\text{O}$  in the two caps. Dehydration of another  $\sim 10\%$  of the upper 300km could have released enough  $\text{H}_2\text{O}$  to develop a  $\sim 1\text{--}2\text{km}$ -thick global permafrost layer, assuming saturated 25–50% pore spaces. Much of the  $\text{H}_2\text{O}$  ( $\sim 90\%$ ) in the upper few hundred kilometers may remain as water of hydration.

If the upper few hundred kilometers is largely hydrated, volcanism may have occurred in the presence of excess  $\text{H}_2\text{O}$  throughout Martian history. This raises the possibility that melting points may have been depressed by several hundred degrees (Merrill, 1978). Viscosities could have been low, and oxygen fugacities could have been high. Using the Lewis-Weidenschilling estimates of  $\text{H}_2\text{O}$  content, the amount of  $\text{H}_2\text{O}$  released during a melting event would be the equivalent of 1.3–1.6% by volume ( $1 \text{ g cm}^{-3}$  assumed density for  $\text{H}_2\text{O}$ ) and significant local groundwater and ice production could have potentially resulted during eruptions.

The volumes of  $\text{H}_2\text{O}$  produced according to the Wanke and Dreibus model (Table I, column 3) could possibly have been a factor of 6 higher than the Lewis-Weidenschilling model. Wanke and Dreibus proposed, however, that the  $\text{H}_2\text{O}$  would have essentially all reacted with metallic iron in the interior of the planet, followed by escape of  $\text{H}_2$ . A resultant depletion factor for  $\text{H}_2\text{O}$  of  $5.5 \times 10^{-4}$  was proposed, yielding a total of only 11.5ppm  $\text{H}_2\text{O}$ .

The argument by Wanke and Dreibus (1985) that  $\text{H}_2\text{O}$  would react with metallic Fe in the interior is inconsistent with the equilibrium condensation model as proposed by Lewis and coworkers. The latter model argues that accreted solids would have been in equilibrium prior to and during accretion, with iron accreting primarily as  $\text{Fe}^{2+}$  in silicates and in FeS. Negligible Fe metal would have accreted. Reaction of  $\text{H}_2\text{O}$  with Fe metal to oxidize iron would have occurred in the nebula prior to accretion, not in the interior

after accretion. Both models produce similar bulk compositions for the mantle and crust, and both predict large initial accreted abundances of  $H_2O$ . The principal difference lies in the argument for accretion of equilibrium or disequilibrium phases.

The evidence for high oxygen fugacity inferred from the detected presence of  $Fe^{3+}$  in surface pyroxenes and from the analyses of SNC meteorites (Huguenin and Anderson, 1985) is more consistent with the equilibrium condensation model of Lewis and coworkers than with the disequilibrium model proposed by Wanke and Dreibus.

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TABLE I: Mars Composition

	Crust	Mantle and Crust	Mantle and Crust
	<u>Huguenin and Anderson</u>	<u>Lewis-Weidenschilling</u>	<u>Wanke and Dreibus</u>
SiO <sub>2</sub>	44.0% (weight)	43.6-43.9%	44.4%
TiO <sub>2</sub>	0.62	0.16	0.14
Al <sub>2</sub> O <sub>3</sub>	7.3	3.1-3.2	3.0
Cr <sub>2</sub> O <sub>3</sub>	-	-	0.76
MgO	12.0-30.0	31.0-31.2	30.2
FeO	14.5	16.7-17.2	17.9
MnO	-	-	0.46
CaO	5.7	2.9-3.0	2.45
Na <sub>2</sub> O	1.5	1.4	0.50
H <sub>2</sub> O	-	0.44-0.47	*2.7

\* Initial estimated accreted  $H_2O$  abundance 2.1% of planet and mantle plus crust comprises 78.3% of planet. All  $H_2O$  assumed to be accreted within mantle and crust.

THE EVOLUTION OF  $\text{CO}_2$  ON MARS; R. Kahn, Dept. of Earth and Planetary Sciences, and McDonnell Center for the Space Sciences, Washington University

The budget and evolution of  $\text{CO}_2$  on Mars, and in particular, the nearness of the current atmospheric  $\text{CO}_2$  pressure to the triple point pressure of water, have eluded explanation. I argue (Kahn, 1985) that  $\text{CO}_2$  could have been precipitated into carbonate rock in the presence of liquid water, perhaps early in Mars history in open liquid, but subsequently in disequilibrium occurrences of moisture in the soil. The overburden pressure of  $\text{CO}_2$  must exceed the triple point pressure of water in some average sense for the disequilibrium mechanism to operate. If the process has functioned to near completion, formation of liquid water on Mars should be difficult but not necessarily impossible, in agreement with a theoretical assessment of current Mars conditions. This idea has profound implications for the climate history of the planet; it suggests that to first order, the climate has evolved in a linear rather than a cyclic manner.

Reference: Kahn, R., Icarus 62, 175-190, 1985.

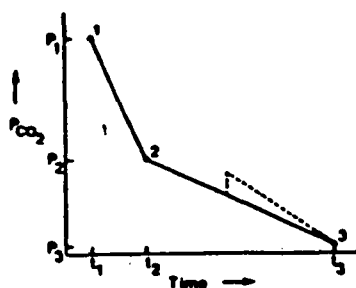


FIG. 3. A schematic illustration of some possible scenarios for the evolution of  $P_{\text{CO}_2}$  (See Table III). The dashed line shows the effect of a rapid outgassing event.

TABLE III

SOME POSSIBLE SCENARIOS FOR THE EVOLUTION OF  $P_{\text{CO}_2}$ \*

	$P_{\text{CO}_2}$ (mbar)		Age (by ago)
$P_1$	140-3000	$t_1$	3.5-4.5
$P_2$	600-2000	$t_2$	>3.1
$P_3$	6-8	$t_3$	>0.0

\* See Fig. 3.

LOSS OF FINE-SCALE SURFACE TEXTURE IN VIKING ORBITER IMAGES DUE TO ATMOSPHERIC OBSCURATION, AND A REASSESSMENT OF LATITUDINAL DEBRIS MANTLING ON MARS;\* Ralph Kahn, Edward Guinness, and Raymond Arvidson, McDonnell Center for the Space Sciences, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130

The absence of fine-scale surface features in Viking Orbiter images must be interpreted with caution. A reduction in contrast due to the presence of atmospheric haze will preferentially obscure small features. Two sets of images of the same region, taken with similar viewing geometry but under different atmospheric conditions, allow us to demonstrate that a single scattering model quantitatively accounts for the effects of the atmosphere. Craters five to seven times the size of the camera picture element should be resolved in Viking Orbiter images if the atmosphere is clear. When atmospheric haze effects dominate, larger craters are obscured and crater size frequency distributions appear to be depleted in small sized craters in a predictable way. Twelve crater size-frequency counts in the northern hemisphere behave in the manner predicted for hazy conditions. Their characteristics also follow the pattern of increasing atmospheric opacity with latitude in spring and summer deduced from other measurements of cloudiness. Loss of surface resolution due to the nearly ubiquitous atmospheric obscuration in the northern mid to high latitudes makes it difficult to assess, with existing images, the validity of suggestions that fine-scale surface features have been preferentially degraded by surface processes. However, the atmosphere in the southern mid and high latitudes is relatively clear during autumn and winter, and a preliminary review of existing image data suggests that features with sizes down to five to seven picture elements can be detected in this region. No evidence for a recent circumpolar debris mantle can be found in the southern hemisphere data. Because the smallest craters that can be resolved in Viking images are

several tens of meters in diameter, we cannot rule out the occurrence of debris deposits less than a few tens of meters thick, regardless of atmospheric clarity.

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\* Icarus, in press, 1985.

# MARTIAN DUST STORMS AND CLIMATE CHANGE

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The characteristics of large dust storms on Mars are now fairly well understood. Most such storms occur in one of the following situations.

(i) During the spring recession of the south polar  $\text{CO}_2$  cap, strong cap outflow winds produce frequent dust storms in the latitude belt adjacent to the polar cap edge (Type I dust storms). (ii) Close to perihelion, large dust storms occur in the southern hemisphere subtropical highlands (Type II dust storms). These storms undergo a marked diurnal cycle, which is indicative of control by the diurnal cycle of convection and/or diurnal thermal tides. When sufficiently widespread and intense, dust from these storms can be carried to high altitudes and spread globally. Such global storms do not occur in every perihelion season, however. (iii) During northern winter periods when global dust storms are not active, traveling baroclinic waves frequently produce transient winds that raise dust in the 20-50N latitude belt (Type III dust storms). These storms are particularly frequent in lowland regions of the northern mid-latitudes (1,2).

Based on observations of winds and grain displacements at one of the Viking lander sites, saltation threshold wind speed at the 1.6 meter wind measurement level is about  $30 \text{ ms}^{-1}$  (3). Extrapolating to the surface and assuming roughness lengths in the reasonable range 0.1-1.0 cm, the threshold friction velocity  $u_{*t}$  is  $1.5\text{--}2.5 \text{ ms}^{-1}$ , a range that is quite consistent with predictions based on theory and laboratory experiments (4). Evidently this threshold is exceeded fairly frequently in the seasons and regions of the three types of dust storms. The Type III dust storms are of particular interest. The strongest winds measured by the Viking landers occurred during these storms. They may be responsible for some systematic differences in aeolian features in the northern and southern hemispheres, for example: the comparatively greater extent and regularity of the north polar laminated terrain. These storms may be less intense in the south than in the north during all phases of the precessional cycle because of the channeling effect of the zonally symmetric lowland region in the northern midlatitudes which has no southern counterpart.

These observations raise the question: what would the aeolian signature be for a past epoch of much enhanced surface pressure? The average aeolian erosive power at a particular location is proportional to the product of  $u_{*t}^3$  and the frequency of occurrence of dust storm events. Since such events occur in the tail of the wind frequency distribution, this frequency is likely to be of the form  $\exp[-(u_{*t}/\bar{u}_*)^n]$  where  $\bar{u}_*$  is the climatological mean friction velocity and  $n \sim 2$ . According to saltation theory  $u_{*t}$  varies as  $p^{-1/2}$ , while dynamical theory suggests that  $\bar{u}_*$  varies as  $p^{-1/3}$ , where  $p$  is surface pressure. The general conclusion that can be drawn from combining these factors is that a period of greatly increased surface pressure would probably have been associated with much more widespread and more nearly uniform aeolian erosion rates than occur at present, but probably not with much more intense aeolian erosion in the presently active sites. Thus, if an ancient epoch of much higher surface pressure occurred in the past and extended over a long period, its signature might be

## MARTIAN DUST STORMS

C. B. Leovy

found in a planet-wide pattern of aeolian activity similar to that found now in the most active areas. Acknowledgement: This research was supported in part by NASA Grant NSG-7085.

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## EARLY VOLATILE ELEMENT INVENTORIES ON MARS

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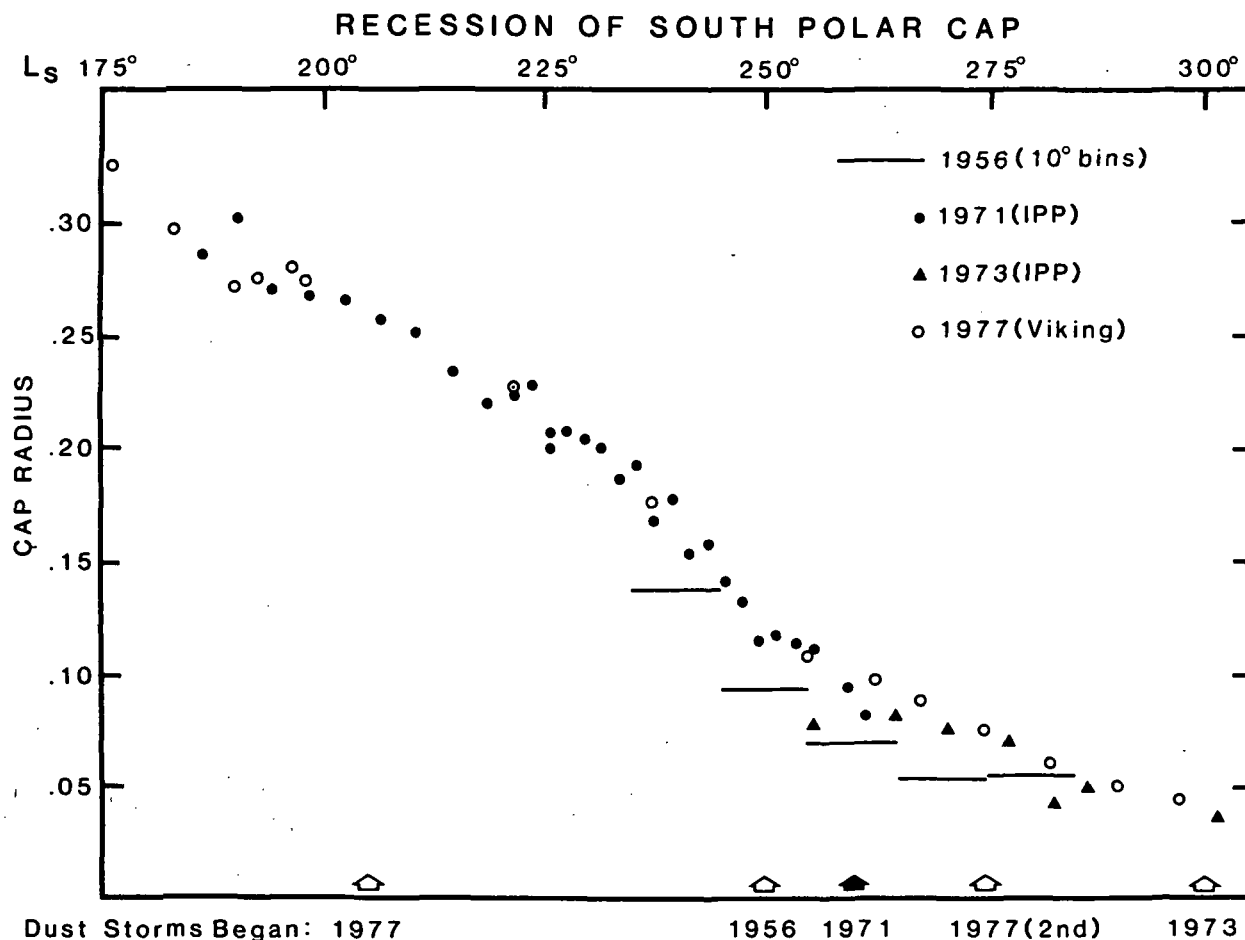
A survey of the major sources of volatiles on the terrestrial planets and the main loss mechanisms for atmospheric gases strongly supports the idea of a dramatic decline in the total atmospheric mass of Mars. We present an assessment of plausible condensation and accretion scenarios for the vicinity of Mars for the purpose of estimating the "primordial" endowments of volatile elements in the planet. The present elemental and isotopic composition will be interpreted in terms of outgassing and impact-driven explosive blowoff. We claim that these processes are powerful and sensitive determinants of the present atmospheric mass and of most features of the present isotopic composition of the volatile elements.



MAJOR DUST STORM ACTIVITY AND VARIATIONS IN THE RECESSIONS OF MARS' SOUTH POLAR CAP; Leonard J. Martin, Planetary Research Center, Lowell Observatory; and Philip B. James, University of Missouri, St. Louis, and Lowell Observatory.

The possibility that large dust storms could alter the recession rate of the seasonal South Polar Cap was discussed by James et al. (1979). However, the nature of this relationship between cap recessions and major dust storms is uncertain. There are few reliable cases where storms may be related to cap recessions, and these do not follow a recognizable pattern. Possible effects that these phenomena may have upon each other are probably dependent upon the size and intensity of the storms and their timing relative to the cap's recession. We have seen the dust storm "season" expand to more than one-third of the Martian year, and it presently includes most of the South Cap's recession period. The dust storm "season" could well be even longer since it coincides with the intervals when Mars is closest to the Earth and therefore easiest to observe. All photographically confirmable major storms have occurred when Mars' apparent diameter was more than 19 seconds of arc. The number of these storms is small (Martin 1984), and it is probable that they do not occur during this "season" every Martian year.

James et al. (1979) showed that the South Cap's recession rates do vary, thus settling a long debate (Slipher 1962). We therefore re-examined the historical records beginning with 1905 (Fischbacher, Martin, and Baum 1969). Of the four pairs of Mars apparitions that covered significant portions of the regression curve, we found that the cap's recession varied substantially from the median during three years. The cap recession fell behind schedule for a while during both 1939 and 1954, neither of which is known to be a year of major storms. During 1956 the cap had already begun to recede at a faster-than-median rate when the planet-encircling storm started (James and Lumme 1982). Conversely, in 1977 the earliest of two planet-encircling storms started well before the cap recession began to deviate from the median; in this case, the recession was found to be slower than usual (James et al. 1979). Both the 1956 and 1971 deviations occurred during about the same seasonal interval which includes the steepest portion of the recession curve. The 1971 planetwide storm began later in the season than either the 1956 storm or the early 1977 storm, obscuring the cap from further Earth-based observations. Mariner observations show that after this storm had cleared the cap was receding ahead of the median curve. Each of these cases appears to be a unique situation, leaving us with no statistical constraints to speculate on various causes and effects. Correlations probably exist, but the data are too thin to determine what they really are. It also appears that some variations in the recessions may not be related to dust storm activity.



The radius of Mars' south polar cap is plotted as a function of the areocentric longitude of the Sun from several data sets. Data for 1956 were derived from Fischbacher, Martin, and Baum (1969). Data for 1971 and 1973 were measured on International Planetary Patrol films by James and Lumme (1982). Viking data are from James et al. (1979). The planet-encircling dust storms and planetwide (solid arrow) dust storm that occurred during these years are shown across the bottom.

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UPDATE OF THE ANDERS-OWEN MODEL FOR MARTIAN VOLATILES. T. Owen, Department of Earth and Space Sciences, State University of New York, Stony Brook, NY 11794.

Our original paper describing a model invoking a meteoritic source for Martian and terrestrial volatiles (1) is now nearly ten years old. Perhaps the most dramatic new information and ideas that have occurred since then are the detailed data concerning composition of the atmosphere of Venus resulting from Pioneer Venus and Venera probes (2), the suggestion that SNCC meteorites originated on Mars (3) and the evocation of large scale impacts to explain, e.g., the origin of the Earth's moon (4). I shall offer a personal appraisal of the significance of the first and third of these items for the Anders-Owen model. The second is discussed in detail by R. Pepin at this conference. I only wish to add here that the precision of  $\pm 10\%$  on  $^{36}\text{Ar}/^{38}\text{Ar}$  in the Martian atmosphere cited in (5) is a mistake. This ratio was only determined to lie within a range of 4 to 7, as originally reported (6). Hence the argon isotope data do not exclude a Martian origin for the SNCC meteorites.

A basic tenet of our original model is that the volatile inventories of the three inner planets with atmospheres were established by meteoritic bombardment. This assumption was buttressed by the similarity of the noble gas abundance pattern in the atmospheres of Earth and Mars and in the so-called planetary pattern in meteorites. At the time of our paper, the available information about volatile abundances on Venus was entirely consistent with this approach.

The new Venus data support the idea that volatiles were delivered to Venus from a source (or sources) at larger solar distances by demonstrating that Venus once had oceans of water (7). However, the noble gases in the atmosphere of Venus were found to differ from the predictions of our model in two important respects: the abundances of neon and argon per gram of planet are excessively high, and the pattern of noble gas abundances is distinctly non-planetary. That is, while  $[\text{Ne}]/[\text{Ar}]$  is similar on Venus and Earth,  $[\text{Ar}]/[\text{Kr}]$  more nearly resembles the solar pattern. Despite these differences, the amounts of carbon and nitrogen presently in the atmosphere of Venus are close to those outgassed by the Earth over its geologic history. One question we obviously need to answer is which of these apparent agreements is/are telling us something significant and which is/are simply coincidence(s)?

Cameron (4) has emphasized the importance of large scale impacts on the atmospheric evolution of the terrestrial planets. In particular, he points out that formation of the moon by a Mars-sized impact with the Earth will strip off any early atmosphere our planet had produced. This atmosphere must then be replaced by infalling material. Mars, being closer to the asteroid belt, would have been subjected to bombardment for a longer period. Being smaller, it could lose an outgassed atmosphere more easily than Earth. These two features could account for the much thinner atmosphere this planet presently possesses, despite the fact that Mars formed in a more volatile-rich part of the solar nebula.

Model for Martian Volatiles  
Owen, T.

This new perspective is still consistent with the basic feature of the meteoritic model for the origin of inner planet atmospheres. It is simply necessary to consider the equilibrium between losses of volatiles - by large impacts, and gains - from small impacts. But Venus remains a problem. Perhaps a large impact occurred but no moon was formed. Or perhaps the present near agreement in the outgassed C and N on Earth and Venus is mere coincidence, with large amounts of both of these elements dissolved in both planets' cores.

The problem of the noble gas abundances on Venus requires a separate solution. One interesting possibility is an impact by an icy planetesimal carrying argon and the other heavy noble gases in solar proportions. An object approximately 400 Km in diameter is required. Neon is not trapped by ices forming at low temperatures (8), thus it must be supplied from another source, presumably the solar wind. For the solar wind to be responsible, however, one needs a 100% capture cross-section and an average flux 10X the present value over the lifetime of the solar system. Alternatively, the flux of material given off during the first  $\sim 10^6$  years after the sun "turned on" would have been adequate to supply the neon, if the planet or the precursor planetesimals were there to collect it. The ratio of  $^{20}\text{Ne}/^{22}\text{Ne}$  ( $11.9 \pm 0.7$  [2-1982]) indeed implicates the solar wind as a major source of the neon on Venus.

The Earth must also have been bombarded by icy planetesimals. To keep this model consistent, one would have to postulate that only Venus was struck by such a large icy object and/or that the record of early icy bombardment on Earth was removed by the same impact that formed the moon.

Studies of Halley's Comet planned for 1986 may finally tell us what volatiles in what abundances were delivered to the inner planets by icy planetesimals. These would be an addition to the meteoritic complement. Comets cannot have supplied all of the volatiles because the ratios of C/N/Ar in ices formed in the solar nebula should be very different (more nearly solar) than those found in the planetary atmospheres.

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NON-LINEAR FROST ALBEDO FEEDBACK ON MARS: OBSERVATIONS AND MODELS  
 D. A. Paige (Calif. Institute of Technology, Pasadena, CA) and H. H. Kieffer (U.S. Geological Survey, Flagstaff AZ)

Recent analysis of Viking Infrared Thermal Mapper (IRTM) observations of the north and south polar caps of Mars indicates that they show a systematic tendency to become brighter with increasing rates of incident solar radiation (1). Frost deposits that receive negligible diurnally averaged insolation have albedos of approximately 0.55. Frost deposits that receive the maximum possible diurnally averaged insolation (at the south pole near summer solstice) have albedos of approximately 0.8 (2). The tendency for frost albedos to increase with increasing incident solar radiation has been observed as a function of latitude at fixed seasons (3) and as a function of season at fixed latitudes (1,2).

It is suggested that the insolation-dependent reflectivities of Martian CO<sub>2</sub> frost deposits is caused by dust particles sinking into the frost. Model calculations indicate that dust particles sink to equilibrium depths below the tops of the frost layers on a time scale of a few hours. Equilibrium depths increase with the rate of insolation because frost sublimation rates in dusty subsurface layers and dust free near surface layers are not proportional. The degree to which frost reflectivities are influenced by total dust content is presently unclear. The validity of the present model calculations can be tested experimentally.

The dust sinking hypothesis can explain some of the more puzzling aspects of the present Martian climate. Viking Orbiter observations have shown that CO<sub>2</sub> frost is stable throughout the year at the south pole but not at the north. Although both poles receive the same total insolation over the course of a year, the present orbital configuration causes peak insolation rates to be higher at the south pole than at the north pole since Mars is closer to the sun during southern spring and summer. If the albedos of seasonal CO<sub>2</sub> frost deposits increase with increasing rates of insolation, then the south pole will be the favored location for a permanent CO<sub>2</sub> deposit. Measured surface pressures at the Viking landing sites show a remarkable repeatability from year to year despite significant interannual variations in the occurrence of global dust storms (4). If the albedos of Martian seasonal frost deposits are relatively insensitive to their total dust content, then the year to year repeatability of seasonal pressure variations can be explained. (The effects of insolation-dependent frost albedos on Martian seasonal pressure variations will be presented at the workshop.)

The dust sinking hypothesis has important ramifications for the long term climate of Mars. If frost albedos increase with increasing rates of incident solar radiation, then the sensitivity of the Martian cap-atmosphere system to changes in insolation due to astronomical variations in the planet's orbital and axial elements will be substantially reduced. Model calculations show that if the present relationship between insolation and frost albedo is maintained, then surface pressures sufficient to

## FROST ALBEDO FEEDBACK

Paige, D. A. and Kieffer, H. H.

suspend dust particles could be achieved for every possible combination of Martian orbital and axial elements. It will be interesting to discuss whether the notion of a self regulating Martian climate is in direct conflict with any hard evidence for substantial climatic changes on Mars over the past billion or so years.

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VOLATILE INVENTORY OF MARS. R. O. Pepin, School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

Elemental and isotopic abundances of atmophilic elements trapped in the glassy lithology of the EETA 79001 shergottite are in good agreement with Viking measurements of martian atmospheric composition. (The  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio may be an exception, but the quality of the spacecraft data is such that it is unclear whether the apparent discrepancy is significant). The data base for the 79001 glass is quite extensive: results from several noble gas studies(1-6), and from nitrogen(4,5) and carbon(7) analyses, are now available. The geochemical case for EETA 79001 in particular, and the SNC meteorites in general, as Mars derivatives is further strengthened by the fact that absolute number densities (particles per unit volume) of gases trapped in the 79001 glass and gases in the present-day lower martian atmosphere are essentially identical. This remarkable observation, first made by Ott and Begemann(8), certainly sets stringent boundary conditions on the trapping mechanism, but these conditions are much more credible than the incredible coincidence that must be invoked in any scenario of non-martian origin.

This direct evidence for origin of the SNC meteorites on Mars, and for trapping of an unfractionated sample of martian atmospheric gases in the 79001 glass, provides a reasonable basis for comparing the martian and terrestrial atmospheres with more precision than that afforded by the Viking data set. ISOTOPES. The  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio, not measured by Viking, appears to be about 10; the average of two estimates(5,6) from the 79001 glass is  $10.1 \pm 0.5$ , close to the terrestrial ratio of 9.8. Kr and Xe compositions are non-chondritic; they are generally earth-like except for a small mass fractionation effect favoring the light isotopes, a much higher relative abundance of  $^{129}\text{Xe}$ , and indications that the component structures of martian and terrestrial Xe may be somewhat different. There is no evidence for measurable amounts of fissiogenic Xe from either U or Pu in the martian atmosphere. Ar composition is anomalous: the trapped  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio of  $\approx 4$  in the 79001 glass is strikingly lower than the values near 5.3 that characterize both the earth and major meteoritic gas carriers. A primordial martian ratio of 5.3 could in principle have been altered by some planet-specific process (e.g., cosmic-ray spallation of surface materials) operating over geologic time, but we have not yet found one that works. ELEMENTAL ABUNDANCES. There is a remarkable empirical relationship between martian and terrestrial abundances ( $[A]$ ) of  $\text{N}_2$ ,  $\text{CO}_2$ ,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  in observable volatile reservoirs (atmosphere at maximum pressure for Mars, and atmosphere, hydrosphere, biosphere, and sedimentary rocks for Earth), which can be expressed as  $[A_M] = 1.27 \times 10^{-4} [A_E]^{0.865}$ . The average deviation from this correlation for the six volatile species is  $\sim 25\%$ . If the relationship is also valid for  $\text{H}_2\text{O}$ , then the known martian water reservoir, the north polar cap, would contain an average of  $\sim 150$  m of  $\text{H}_2\text{O}$  ice over its area, equivalent to a planet-wide 75 cm water column. The radiogenic gases  $^{40}\text{Ar}$  and  $^{129}\text{Xe}$  fall well off this correlation, in the direction of higher abundances for Mars.

Relative elemental abundance ratios of noble gases in the martian and terrestrial atmospheres, expressed as  $[M/^{130}\text{Xe}]_M / [M/^{130}\text{Xe}]_E$  for  $M = ^{84}\text{Kr}$ ,  $^{36}\text{Ar}$  and  $^{20}\text{Ne}$ , decrease with decreasing mass in a functional relationship that is fit very well by a variety of mass fractionation mechanisms. This suggests that Mars, or its protoplanetary feedstock, has suffered mass-dependent noble gas losses in comparison with Earth. Losses can be calculated assuming either Aston-type or Fick's Law diffusion: they range from  $\sim 80\%$  for Xe to  $\sim 95\%$  for Ne. The noble gas inventory for Mars, prior to the onset of diffusive loss, would

## VOLATILES ON MARS

Pepin, R. O.

then have been 1/15 of the terrestrial inventory. This factor is in good accord with McElroy et al.'s(9) range of estimates for the initial martian N<sub>2</sub> abundance. Extended to CO<sub>2</sub> and H<sub>2</sub>O, initial (and present?) martian abundances would have been about 0.6 bars and 90 m, respectively. The noble gas calculation assumes that gases initially lost from the planetary material by diffusion escaped from the atmosphere, perhaps in an H<sub>2</sub>-driven hydrodynamic blowoff(10); that the fractionated residual reservoir from which these gases derived subsequently outgassed, and its noble gases were retained in the present atmosphere; and that a large fraction of the earth's nonradiogenic noble gas inventory is in its atmosphere. Other scenarios are possible. We have no way to address quantitatively the factor 15 lower "initial" martian volatile inventory, compared to Earth. It may be that these volatiles as well were lost in blowoff(10), that they were never present, or that they remain in the interior, sequestered in an extensive undepleted mantle untapped by outgassing processes over the life of the planet.

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LONGEVITY OF A DENSE CARBON DIOXIDE ATMOSPHERE ON MARS; James B. Pollack, Space Science Division, NASA-Ames Research Center, Moffett Field, CA. 94035

There are several pieces of evidence that suggest that Mars may have had a warmer and wetter climate during its early history. This evidence includes the ubiquitous occurrence of dendritic gullies in the heavily cratered uplands of the southern hemisphere and the morphological characteristics of impact basins (P. H. Schultz, this document).

Large amounts of carbon dioxide in the early Martian atmosphere represent the most likely way of achieving the necessary greenhouse warming to raise the surface temperature on early Mars above the freezing point of water (1). Surface pressures on the order of 1 bar are required in this case, i.e., a two-orders of magnitude increase in the amount of atmospheric  $\text{CO}_2$  over the current content.

A 1 bar  $\text{CO}_2$  atmosphere is not inconsistent with estimates of Mars' volatile inventory (c.f. R. Pepin, this document). However, the occurrence of liquid water on the surface of early Mars would promote the formation of carbonate rocks at the expense of the atmospheric  $\text{CO}_2$ . Could a large  $\text{CO}_2$  atmosphere last a geologically interesting period of time ( $10^9$  years) to account for the formation of the older gullies and the characteristics of the Martian basins?

I have used characteristics of the  $\text{CO}_2$  geochemical cycle on Earth to answer the above question. In particular, I have scaled the chemical weathering rates on Earth of carbonate rock formation to allow for the effects of atmospheric pressure, temperature, rock cation content, solar radiation, and the surface area covered by liquid water. These calculations suggest that a 1 bar atmosphere on early Mars would be eliminated in about  $10^7$  -  $10^8$  years by carbonate rock formation, in the absence of recycling these rocks back to  $\text{CO}_2$ . While such time scales are quite large, they are probably not large enough to account for the geological data of interest.

I have therefore investigated the possibility of recycling carbonate rocks on early Mars. Global scale volcanism offers an attractive way to accomplish this. Carbonate rocks could be decomposed either by coming into contact with hot lava or by being buried by colder lava to depths where the temperatures are high enough for decomposition ( $\sim 750$  K). Using surface heat flux as a constraint on the rate of volcanism, I find that the recycling time scales are comparable to the weathering time scales on early Mars. Thus, a dense  $\text{CO}_2$  atmosphere could be sustained on early Mars for time scales of  $10^9$  years by the recycling of carbonate rocks engendered by global volcanism. At later times in Martian history, the rate of volcanism is expected to decline and to become more regional in scale. Both these changes would make recycling much less effective and hence the dense  $\text{CO}_2$  atmosphere would be lost.

The above hypothesis may be tested by searching for the presence of carbonate rocks on Mars. R. Kahn has independently advocated searching for carbonate rocks on Mars to help verify his hypothesis that carbonate rock formation on Mars is the key determinant of the present atmospheric pressure at the surface (2).

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THE MARTIAN ATMOSPHERE BEFORE AND AFTER THE ARGYRE IMPACT. P.H. Schultz, Dept. of Geological Sciences, Brown University, Box 1846, Providence, RI 02912.

The early history of the martian atmosphere is recorded in the ancient cratered terrain. Ancient narrow valley networks indicate fluid flow but debate remains concerning their precise mode of origin: rainfall drainage under atmospheric conditions different from today (1,2); melting beneath a global snowfall (3); or subsurface release of water and ground sapping (4,5). Martian narrow valley networks appear to represent immature drainage systems more analogous to sapping processes on the Earth (4,5), thereby weakening the need for an early stage of high atmospheric temperatures and pressures conducive for rainfall. It is repropose here, however, that different climatic conditions did exist during the first 0.5 by and that the inferred sapping by melting of buried ices reflects a relatively late-stage process which followed up to about 3 by. The basis for this proposal principally centers on: (a) the gradation of ancient impact basins and other early landforms; (b) the change in drainage density and style following the Argyre impact; and (c) the change in basin ejecta emplacement style after the Argyre impact.

Ancient Impact Basins: Early studies concluded that large impact structures (diameter >200 km) were deficient relative to the Moon and Mercury (6,7). Recent studies, however, document a much larger inventory of subtle but unmistakable impact basins (8,9). The identification of such structures is based on recognition of not only the familiar primary landforms used for the Moon (concentric massifs, scarps, and ridges) but also secondary landforms including topographic and structural diversion of drainage patterns, concentration of plain units, and diversion of prominent structural patterns. In certain regions of the ancient cratered highlands, the number density of impact basins exceeds the Moon. Consequently the deficiency in other regions is not believed to reflect a low impact flux but a much higher gradation rate early in martian history. The furrowing and channeling of ancient basin massifs and ejecta facies indicate that the high gradation rate is at least in part related to the formation of narrow valley networks.

A second clue to different atmospheric conditions in the past comes from the absence of basin secondaries. On the Moon and Mercury, numerous large secondary craters surround large craters and basins with the largest approaching 5-7% the diameter of the parent crater. On Mars, only basins smaller than 200 km in diameter have identifiable secondaries beyond the continuous ejecta deposits. The 1900 km-diameter Argyre basin (measured to the outer ring scarp) is the only exception with a few 20-30 km secondaries. The condition of these very few secondaries indicates that this basin is relatively well preserved, yet the extensive radial lineations and vast secondary crater fields similar to those around Imbrium and Orientale on the Moon (see 10) are missing. If Mars had the same atmospheric pressure as it does today, then such an atmosphere would not have prevented the radial facies and secondaries from forming -- just as secondary craters were produced around numerous other more recent martian impact craters smaller than 200 km in diameter. A possible explanation invokes a much higher atmospheric pressure that either prevented secondaries from forming due to high aerodynamic pressures during ejecta re-entry or violent post-impact winds that quickly modified the ejecta emplacement process. Both processes have been documented experimentally and predicted theoretically (11).

## BEFORE AND AFTER ARGYRE IMPACT

Schultz P. H.

It remains equivocal whether or not pre-Argyre impact basins once had the characteristic secondary crater fields. However, if narrow valley networks represent an immature drainage system -- thereby indicating a limited erosional capacity, then it is paradoxical that these valleys 1-2 km in width could be preserved today while secondary craters 10-30 km in diameter have been destroyed. A more reasonable scenario invokes a higher erosional capacity early in martian history with a change in conditions leading to the formation of presently preserved narrow valley networks. Such a scenario is supported by a documented change in the style and density of narrow valley networks soon after the formation of the Argyre impact (12).

Conclusions: The impact basin record on Mars suggests that atmospheric conditions during and prior to the formation of the Argyre impact were dramatically different than today. This conclusion is based on: (a) the heavily eroded state of pre-Argyre basins; (b) an incomplete basin population probably not related to a deficit of impactors; (c) an inverse relation between the existence of crater/basin secondaries and density of narrow valleys; (d) the absence of typical basin ejecta facies around Argyre that should have been produced and preserved; and (e) the dramatic decrease in drainage density and change in drainage style after the Argyre impact. It is further proposed that the present record of narrow valley networks is dominated by immature drainage patterns that are only the last stages of a more extensive period of gradation contemporary with the formation of pre-Argyre impact basins.

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**VALLES MARINERIS AS KARST: FEASIBILITY AND IMPLICATIONS FOR MARTIAN ATMOSPHERIC EVOLUTION.** J.R. Spencer and S.K. Croft, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, 85721

The origin of the vast Martian equatorial canyon system, Valles Marineris, is still a mystery. There is much evidence for tectonic control (1), but the blunt, irregular or closed shape of many of the troughs, and the abundant collapse features, indicate that the loss of material cannot be due mostly to simple downdropping of the crust along faults (2).

The collapse features (chains of pits developed along small graben, apparently coalescing to form linear depressions which then enlarge into full size canyons) have led many authors to suggest the removal of subsurface material as a major contributor to canyon formation. Sharp (3) suggested that ground ice removal led to collapse and canyon formation or enlargement. A serious problem, however, may be the difficulty of maintaining such extreme topography in an ice-rich crust.

Hebes Chasma, for example, has a depth of 7 km, and as it is closed, material cannot have been moved out of it laterally except by wind, which is considered unlikely (3,2). Assuming none of the non-ice has left, if the crust is more than 50% ice by volume, the ice must have been removed to a depth of more than 14 km, or 7 km below the present floor. This is geologically very hard to justify. We thus assume a lower limit of 50% ice in the upper crust, if ice removal is significant in canyon formation.

The melting point of ice near the Martian equator is probably achieved at a depth of only 1 km (4), which in itself makes a very ice-rich crust unlikely as the canyons are much deeper than this. However, we assume that the canyon walls contain ice close to, but below, the melting temperature. The viscosity of pure ice at 270K is between  $10^{15}$  and  $10^{16}$  poise (5), and the viscosity of a 50/50 (by volume) ice-silicate mixture is less than 100 times greater than pure ice (6,7), so on the ice-removal hypothesis, the viscosity of the canyon wall material is likely to be no more than  $10^{18}$  poise. The timescale for collapse of 10 km - amplitude Martian topography in material with this viscosity is of the order of 50 years! The viscosity argument does not rule out models in which the ice is a minor component which acts as a binder, whose loss causes the material to lose cohesion so that it can be removed by wind. Such models face the problem of reducing all the canyon wall rock to dust size prior to wind removal, however.

We propose an alternative method of canyon excavation, in which much of the subsurface rock is carbonate, and is dissolved by groundwater in a manner analogous to terrestrial karst. Subsurface dissolution of carbonate and subsequent collapse of cavities thus formed, followed by continued enlargement of the depressions by further solution, would explain the canyon morphology just as well as collapse due to ground ice removal, without the problem of maintaining the topography against viscous flow.

Some models of Martian evolution (e.g. 8 and this report) propose an atmospheric history in which  $H_2O$  and  $CO_2$  are largely retained, allowing for the possibility of abundant  $CO_2$ -saturated water on the early surface. Formation of large amounts of carbonate by silicate weathering is then very likely (9,10). Large local deposits of carbonate rock could be built up by migration of water to low regions. If this "wet" phase of Martian evolution ended before the termination of heavy bombardment, which probably occurred around 3.9 b.y., all morphological traces would have been removed. If the entire Valles Marineris region contained a 10 km thickness of limestone, the stored  $CO_2$  would be equivalent to roughly 5 bars atmospheric pressure over the

whole planet, and the uniqueness of the canyon region suggests that it might contain the bulk of the present subsurface carbonate.

The dissolution and transport of the supposed carbonates requires an active groundwater system. Transport of materials in suspension in groundwater, possibly connected with a system of lakes within the major canyons (11), has been invoked by Carr (2) to explain the collapse features and the layered deposits in the canyons. Transport of carbonates in solution is equally feasible.

The ultimate fate of the vast quantities of material that must be removed to excavate the canyons is a difficult question, though no more difficult for this theory than for competing ones. The dissolved carbonate could be removed slowly by downhill percolation of carbonate-saturated groundwater towards the channelled terrain to the east of the canyons, and deposited either in mega-regolith pore spaces or near the surface. Because of the limited solubility of carbonate in water ( $\sim 4 \times 10^{-5}$  by volume for pure water at 0°C in equilibrium with the Martian atmosphere) very active atmospheric recycling of water is required to circulate enough through the canyons to dissolve them. A more attractive possibility is that convection of deep groundwater might dissolve carbonate in the upper crust and re-deposit it at depth in mega-regolith pore spaces in a continuous cycle, without the water ever appearing at the surface. The increase in solubility of carbonate with decreasing water temperature would facilitate downward carbonate transport as part of the convective process.

The spectral features of carbonates have not been seen in either the near-IR reflectance spectrum of Mars (12) or the thermal emission spectrum of dust clouds (13). An approximate upper limit of 5% carbonates in the surface material is indicated (14). It might be expected that carbonates removed from the Valles Marineris area and subsequently re-deposited near the surface would be detectable in the apparently globally-homogenized surface dust layer. However, it may be that the carbonates are diluted below the 5% detection threshold, or are broken down by SO<sub>2</sub> (14). MGC0 observations will be invaluable in helping to resolve this question by providing high resolution maps of surface mineralogy.

In conclusion, the possibility that the Valles Marineris system indicates the storage of several bar's worth of CO<sub>2</sub> in the form of carbonates beneath one portion of the Martian surface is offered for consideration by geologists, geochemists, and atmospheric scientists concerned with Martian evolution. Much of the idea's strength lies in the difficulty of explaining Valles Marineris by other models, but more detailed work on the likely chemistry and circulation of deep Martian groundwater, and mineralogical and topographic data obtained by MGC0, may allow refinement or rejection of the hypothesis on its own merits.

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EARLY EVOLUTION OF THE TERRESTRIAL ATMOSPHERE. James CG. Walker  
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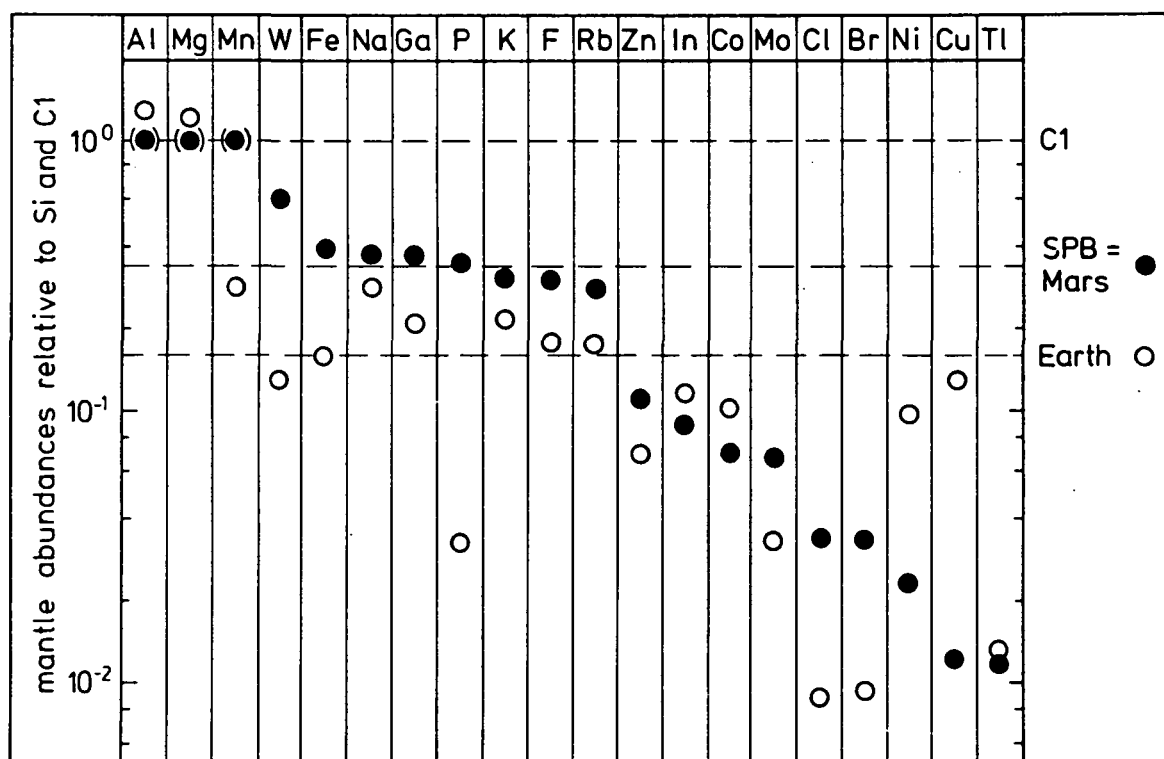
This paper is concerned with the history of release of volatiles from the solid earth. The sedimentary shell today contains too much reduced organic carbon compared with the store of oxidants in sediments, ocean, and atmosphere. It appears either that the gases released from the interior of the earth were at one time significantly more reduced than they are today or else that the exogenic system has lost oxidants, presumably to the mantle. Either conclusion implies that the mantle was at one time more reduced on average than it is now.

Data that relate to the oxygen fugacity in the mantle are consistent with this finding. Parts of the mantle have an oxygen fugacity corresponding to a former equilibrium, before differentiation of the core, with metallic iron. Other parts are more oxidized. Release of reduced gases after core formation would have driven oxygen fugacities in the mantle to values near the QFM buffer, at which the stable form of carbon is graphite or diamond, depending on temperature. The mixing ratio of carbon in any vapor phase at these oxygen fugacities is very low indeed. Release of carbon from the interior of the earth could not have occurred in significant quantities until oxidant was added to the mantle, presumably by subduction of oxidized sediments. The sediments could have been oxidized either as a result of oxygenic photosynthesis or as a consequence of the escape to space of hydrogen, possibly generated by the abiotic oxidation of dissolved iron in surface sea waters.

Because carbon in its zero valence state is not volatile, it is therefore possible that release of carbon-bearing gases from the solid earth to the atmosphere was mediated by the oxidation of the mantle as a consequence of processes occurring at the surface. Gradual release of carbon dioxide is not inconsistent with catastrophic early degassing of most of earth's volatiles. The geologic record of stable isotopes provides qualitative support to this hypotheses. It is possible that on Mars, also, degassing of carbon dioxide has been gradual.

CAN A HIGH ABUNDANCE OF MODERATELY VOLATILE AND EVEN SOME HIGHLY VOLATILE ELEMENTS ON MARS BE RECONCILED WITH ITS LOW ABUNDANCE OF PRIMORDIAL RARE GASES? H. Wänke and G. Dreibus, Max-Planck-Institut für Chemie, Saarstrasse 23, D-6500 Mainz, F.R.Germany.

There is the general consensus that the parent body (SPB) of the SNC meteorites (Shergottites, Nakhilites, and Chassigny) is volatile-rich. Dreibus and Wänke (1984) have estimated the bulk composition of SPB by using analytical data of SNCs and various element correlations observed for these meteorites. They found that the SPB is about 2 to 3 times richer in moderately volatile and volatile elements as compared to the Earth. The bulk composition obtained in this study fits well with the composition of Mars based on limited geochemical and geophysical evidences available. In light of the numerous evidences that Mars is the SPB (Nyquist et al., 1979; Wasson and Wetherill, 1979; McSween and Stolper, 1980; Dreibus et al., 1981; Wood and Ashwal, 1981; Bogard and Johnson, 1983; Becker and Pepin, 1984), we have to conclude that Mars probably is a volatile-rich planet. Dreibus and Wänke (1984) also presented evidence that the SPB = Mars was formed from the same two components from which the Earth was formed. However, the mixing ratio of component A (reduced and volatile-free) to component B (oxidized and volatiles containing) for Mars was found to be 60:40, while for the Earth a mixing ratio of 85:15 was estimated (Wänke, 1981). It was also noted that contrary to the Earth's mantle, all chalcophile elements are drastically depleted in the Mars' mantle as illustrated in the Figure. This led to the conclusion that contrary to the Earth, Mars accreted almost homogeneously.



Sulfur, mainly supplied by component B, and FeNi from component A were thought to be responsible for the formation of a sulfur-rich FeNi alloy. During core formation extraction of the elements from the mantle took place, according to their sulfide-silicate partition coefficients. Assuming a C 1 Fe/Si ratio for the whole planet and a sulfur abundance equal to  $0.4 \times C 1$ , we found a core mass of 21.7 % and a core composition of 77.8 % Fe, 7.6 % Ni, 0.36 % Co and 14.2 % S. Core mass and composition obtained in this way are well within range of the estimate given by Goettel (1981), based on the assumption of a planet with solar proportion of non-volatile elements and the density of Mars.

In order to explain the different types of accretionary scenarios for Earth and Mars, Dreibus and Wänke (1984) suggested that the volatile-free component A formed mainly at and inside the orbit of the Earth, while the oxidized, volatile-containing component B formed in the asteroidal belt. Mars, located at the transition of the region dominated by component A and the region dominated by component B, was thought to have been fed from both components simultaneously and in approximately equal proportions, while in the case of Earth and Venus the material of component B was added only during a late phase of accretion stage and in smaller proportions.

The amount of  $^{36}\text{Ar}$  in the Martian atmosphere per gram of the planet's mass is a factor 100 lower than in any class of unfractionated meteorites (Anders and Owen, 1977). As there can be no doubt that accretion is the most effective degassing stage in the evolution of planets, a huge gas loss from the primitive atmosphere of Mars seems the almost inevitable conclusion. On the other hand, the  $^{36}\text{Ar}$  content of the Venusian atmosphere (von Zahn et al., 1983) exceeds that of the Earth by a factor of about 100, and even exceeds that in any known meteorite. However, it is conceivable that the original gas content of these meteorites was considerably higher but has declined due to gas loss by diffusion during their 4.5 b.y. of history.

In the two component model for Earth (Wänke 1981) and Mars (Dreibus and Wänke 1984), the volatiles are derived from component B. If component B contain primordial rare gases at the C 1 level, the amount of  $^{36}\text{Ar}$  originally supplied was 2300 times higher than what is presently observed in the Martian atmosphere. As the Martian  $^{36}\text{Ar}$  abundance is a factor of 130 below the terrestrial value, an absolute depletion factor of 2300 for Mars would yield a terrestrial depletion factor of 17. If only 15% of component B was added to the Earth (Wänke 1981), a terrestrial depletion factor of 6 is obtained.

So far all attempts to explain the huge differences in the primordial rare gas content of Venus, Earth and Mars have been based on different initial inventories. We instead propose to explain the observed differences mainly by large differences in gas loss during accretion. As discussed by various authors two quite different processes are thought to be of importance for the removal of the primitive atmospheres: 1) Hydrodynamic escape due to presence of large amounts of  $\text{H}_2$  which leads to low values for the mean molecular weight and 2) removal by large impacts. Because of lower gravity, both processes will be more efficient for Mars when compared to Earth and Venus.

Homogeneous accretion as it is proposed for Mars (Dreibus and Wänke, 1984) will not only generate large amounts of  $\text{H}_2$  but will also make impact induced gas loss more efficient, as impacts of bodies from both populations (component A and B) will be effective. In the case of inhomogeneous accretion the oxidized, volatile-containing component B is added only towards the end of accretion and gas loss by impact is restricted to that period. On Earth and Venus, accretional energy leads to formation of huge magma oceans (Kaula, 1979), in which substantial portions of rare gases redissolved and subsequent-



ly were even carried into the solid regions of the highly convecting mantles. On Mars melting occurred only on a much smaller scale as the energy of accretion and core formation per unit mass are about 4 times lower. In this respect we should note, that the amounts of gases redissolved depend on the thickness of the layers which equilibrate with the atmosphere and only to a lesser degree on the gas/solid partition coefficients.

Impact induced fission of the Proto-Earth seems the most likely model for the origin of the Moon (Hartmann and Davis, 1975; Cameron and Ward, 1976; Ringwood, 1979). The mass of the projectile probably considerably exceeded that of the Moon; its impact towards the end of terrestrial accretion will probably have completely removed any atmosphere present at that moment. Clearly gas loss has also to be expected in the case of Venus. However unlike the Earth, Venus was probably not hit late in its accretion history by an object of sufficient mass to form a moon. The observed amounts of primordial rare gases on Venus can be taken as a lower limit of the amounts added. Relative to Venus the Earth has lost  $10^2$ , and Mars  $10^4$  times more of their primordial rare gases. Aside from a low release factor, atmospheric removal by impacts occurring over geologic history (Watkins and Lewis, 1984) could at least in part be responsible for the low  $^{40}\text{Ar}$  content of Mars' atmosphere. The low concentration of  $^{36}\text{Ar}$  on Mars can be brought in agreement with the obviously high concentrations of moderately volatile and volatile elements such as K, Rb, Cl, Br, and Pb, by assuming that the different rare gas concentrations in Venus, Earth and Mars are due to different loss factors during accretion.

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EVOLUTION OF THE ATMOSPHERE OF MARS AS THE RESULT OF  
 ASTEROIDAL AND COMETARY IMPACTS; G. H. Watkins and J. S. Lewis,  
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Energetic impacts can efficiently remove atmosphere from small planets, whereas outgassing from the planetary interior will produce new atmosphere on these bodies. The present mass and composition of the atmosphere of Mars are governed by these and other processes operating over long periods of time. Our recent work indicates that numerous energetic impacts at the surface of Mars have altered the atmospheric composition and at the same time reduced its mass. From our present work we find that these conclusions are dependent on the outgassing history of the early atmosphere of Mars, and to a lesser extent on the impactor population mass and velocity distributions. The contribution of impactor carried volatiles has not yet been explicitly considered in these models, but preliminary indications are that it may play a significant role in the development of the atmosphere.

Thus far our parameterized model has been employed to examine the effects of different impactor populations, temperature, pressure, and molecular weight variations, and outgassing rates on the ultimate fate of the model atmospheres. In each case the model was run for 100,000 impacts and in the majority of these cases the cumulative impactor mass was  $3 \times 10^{23}$  gm or  $5 \times 10^{-4} M_{\text{Mars}}$ . In a majority of the models studied the early atmosphere was removed by the impactor flux on time scales comparable to, but often less than, those previously proposed for the late heavy bombardment. In some cases we have arbitrarily reduced the efficiency of atmosphere removal by limiting the amount of momentum transferred from the impactor to the atmosphere. Even in these cases, a substantial portion of the atmosphere was stripped by 100,000 impacts.

The results of two representative models are illustrated below. In Figure A the isothermal atmosphere has a surface pressure of 0.01 bar, a temperature of 220K, and a molecular weight of 44 gm/mole. In this Figure five cases are depicted: (i) no outgassing (erosion only), (ii) outgassing at a rate of  $10^{14}$  gm between impacts (erosion and accumulation), (iii) outgassing at a rate of  $10^{15}$  gm between impacts (erosion and accumulation), (iv) outgassing at a rate of  $10^{14}$  gm/unit time without impacts (accumulation only), and (v) outgassing at a rate of  $10^{15}$  gm/unit time without impacts (accumulation only). The most distinctive feature in this Figure is the near equilibrium between atmospheric erosion and outgassing in (iii).

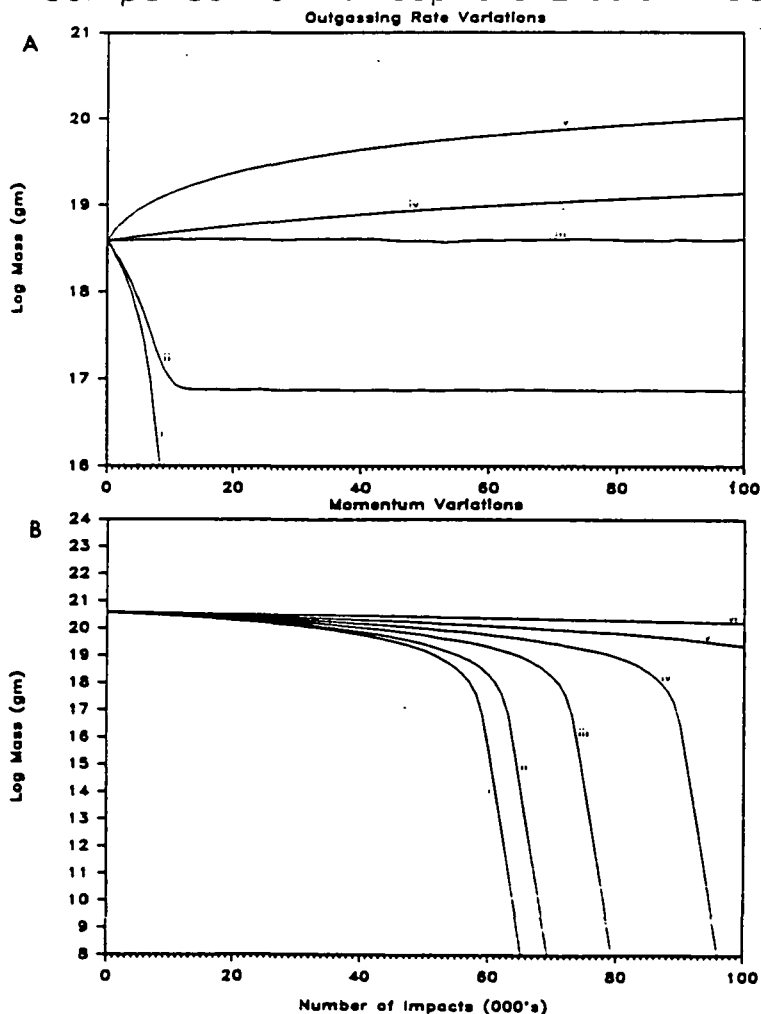
## EVOLUTION OF THE ATMOSPHERE OF MARS...

G. H. Watkins and J. S. Lewis

In Figure B the reduction in efficiency of the impact-induced blowoff is illustrated. In this case the model atmosphere has a surface pressure of 1.0 bar, a temperature of 300K, and a molecular weight of 30 gm/mole. The curves labelled i, ii, iii, iv, v, and vi represent 100%, 90%, 70%, 50%, 30%, and 10%, respectively, of the incoming momentum transferred to the ejecta. Even where only 30% of the impactors' momenta is transferred to the atmosphere, a reduction in the atmospheric mass by nearly an order of magnitude is achieved in 100,000 impacts. This is clearly significant when it is understood that the initial model atmosphere is similar to the present terrestrial atmosphere.

These and other models suggest that the erosion of the atmosphere of Mars by energetic impacts did not stop at the end of the late heavy bombardment, but has continued on to the present, albeit at a reduced rate. The inclusion in the model of impactor carried volatiles and the outgassing, and subsequent blowoff, of primordial and radiogenic rare gases is currently underway.

## Comparison of Atmosphere Erosion Model



MARS; ATMOSPHERIC ESCAPE OF MAJOR VOLATILES J. H. Yatteau  
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Atomic species derived from the major planetary volatiles  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  are currently escaping from Mars. Factors affecting isotopic fractionation due to escape of these species are discussed. Use of isotopic ratios to deduce evolutionary histories and estimate volatile reservoir magnitudes is investigated. Effects of potential climatic variations are considered.

# MARS: A QUANTITATIVE ESTIMATE OF TOTAL $H_2O$ EXCHANGE BETWEEN THE REGOLITH AND THE ATMOSPHERE/CAP SYSTEM OVER OBLIQUITY TIMESCALES

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A quantitative model of the state, distribution and vertical transport of water within the martian regolith is presented. Results include the depth to the permafrost as a function of latitude and obliquity, as well as the abundance of adsorbed  $H_2O$  above the permafrost table, factors which depend upon mass flux of  $H_2O$  into and out of the martian regolith. In addition, in situ phase change of  $H_2O$ , resulting from calorie transport through the martian regolith on a seasonal timescale is predicted.

The calculation accounts for: 1) expected thermal variations at all depths, latitudes and times resulting from seasonal and astronomical insolation variations, 2) variations in atmospheric  $P_{H_2O}$  and  $P_{CO_2}$  resulting from polar insolation variations and regolith adsorptive equilibria, 3) feedback effects related to latent heat deposition and albedo variations resulting from condensation of atmospheric constituents, 4) variations in regolith adsorptive capacity, 5) variations in  $H_2O$  content of the regolith, 6) finite kinetics of  $H_2O$  transport through the martian atmosphere and regolith, and 7) equilibrium phase partitioning of  $H_2O$  between the condensed, adsorbed and vapor phases.

Results suggest that the adsorptive capacity of the regolith is important in controlling the state and distribution of near surface (4 to 5m)  $H_2O$ . Unweathered mafic silicates, of relatively small adsorptive capacity favor development of shallow ground ice at all mid and polar latitudes. Heavily weathered clay-like regolith material, of relatively great adsorptive capacity, results in significantly greater burial depth and far more extensive quantities of adsorbed  $H_2O$ . Withdrawal of long-term ground ice may be irreversible in high-adsorptive capacity regoliths. High capacity regoliths require significant porosity in order to store more  $H_2O$  than can be accommodated in adsorption sites. Withdrawal of ground ice may lead to collapse and subsequent reduction of porosity

to values lower than necessary for the re-insertion of ground ice. Particularly in minerals with inter-layer sites available for  $H_2O$  storage, swelling may exhaust all available pore space before all adsorption sites are full. The total capacity of the mid and high latitude regolith for storage of  $H_2O$  is less dependent on mineralogy or adsorptive capacity however; the regolith is likely to be saturated with  $H_2O$  to within a few tens of centimeters of the surface. Likewise the total mass of  $H_2O$  exchanged between the atmosphere/cap and the subsurface is approximately independent of mineralogy and adsorptive capacity. It is suggested that approximate limits of total exchanged  $H_2O$  range from  $1 \text{ g cm}^{-2}$  to  $20 \text{ g cm}^{-2}$  over the entire surface of Mars. In a high adsorptive capacity regolith, this exchanged mass is likely to reside exclusively in the adsorbed phase when in the regolith. In a low capacity regolith, a majority of the exchanged mass is stored as near-surface ground ice at latitudes ( $\geq 50^\circ$ ). The maximum exchanged equivalent volume is  $3.0 \times 10^4 \text{ km}^3$  of ice. The minimum exchanged equivalent volume is approximately  $1.5 \times 10^3 \text{ km}^3$  of ice. If we approximate the total area of the polar layered terrains as  $2.2 \times 10^6 \text{ km}^2$ , then the deposition of the desorbed  $H_2O$  as continuous coverage over the layered terrain as pure ice would result in a layer between 14m and 70cm thick. If the layered terrain is actually found to consist in part of  $H_2O$  ice, then one likely source of the  $H_2O$  is regolith desorption.

Results also suggest that caloric transport through the regolith, in response to seasonal insolation variations, acts to force in situ phase change of  $H_2O$  over a wide variety of latitude/obliquity conditions. Such seasonal phase behavior is highly dependent on regolith mineralogy. The seasonal cycles of adsorption-freezing which are predicted here may produce geomorphologic signatures not unlike those produce by terrestrial freeze-thaw cycles. Possible examples may be the shallow troughs at the Viking Lander 2 site, and the large expanses of patterned ground at mid-latitudes.

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